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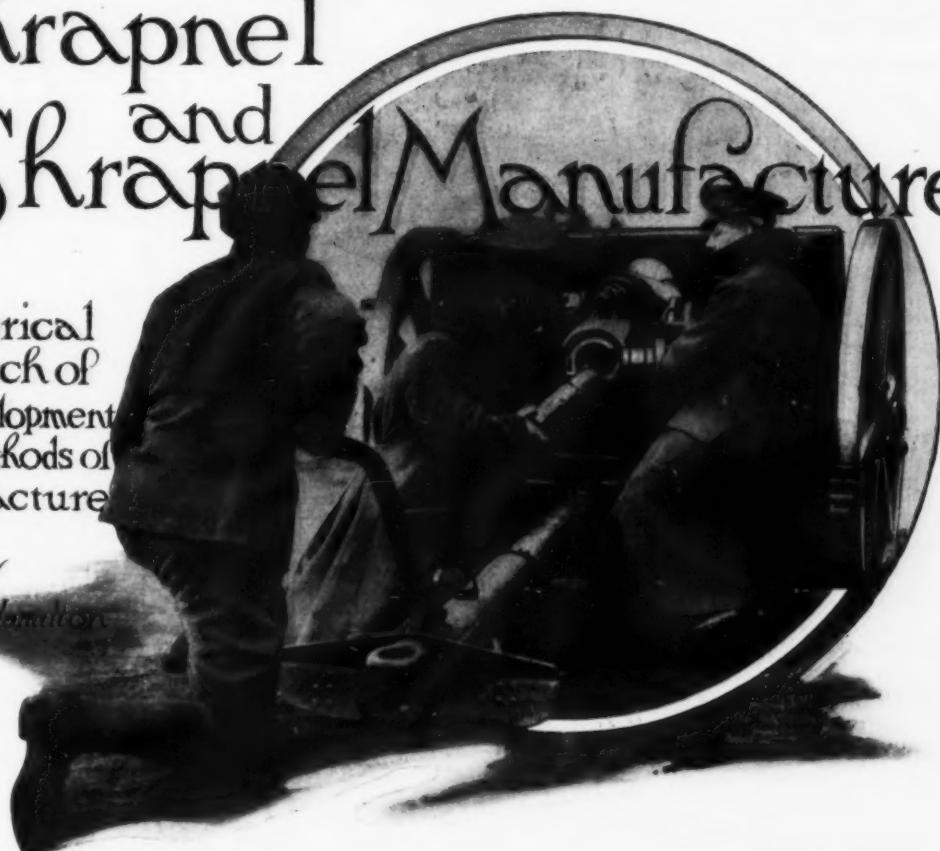
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## Shrapnel and Shrapnel Manufacture

Historical  
Sketch of  
the Development  
and Methods of  
Manufacture

by  
Douglas T. Hamill



**I**N naval coast defense and artillery operations, several types of explosive shells are used; the chief ones are: the armor-piercing shells made to pierce armor plate before exploding; shell exploded by means of a timing fuse; shells exploded by either a timing or percussion fuse; and shells exploded by percussion only. Each different shell has some definite function to fulfil, and is designed for that purpose. For field or artillery operations, the shrapnel and lyddite are the two principal types used. Of these, shrapnel is the most prominent, because of its enormous destructive power and its interesting mechanical construction.

The shrapnel shell was invented in 1784 by Lieut. Henry Shrapnel, and was adopted by the British government in 1808. As is shown at A in Fig. 2, the first shell was spherical in shape and the powder or explosive charge was mixed with the bullets. Although this type of shell was an improvement over the grape and canister previously used, its action was not altogether satisfactory, as the shell, on bursting, projected the bullets in all directions, and there was also a liability of premature explosion. In order to overcome the defects mentioned, Col. Boxer (R. A.) separated the bullets from the bursting charge by a sheet iron diaphragm, as shown at B in Fig. 2. This shell was called a diaphragm shell to differentiate it from the first shell of this type.

In the shell made by Col. Boxer, the lead bullets were hardened by the addition of antimony, and as the bursting charge was small, the shell was weakened by cutting four grooves extending from the fuse hole to the opposite side of the shell. Shells of spherical shape were first fired out of plain bored guns, and upon the advent of the rifled gun it was necessary to add a circular base, which was made of wood and covered with sheet iron or steel to take the rifling grooves. The first

shrapnel shells were made of cast iron, but a later development was to use toughened steel and elongate the body, reducing it in diameter. The diameter of the bullets was also reduced so that a greater number could be contained in a slightly smaller space. The improved shrapnel was also capable of being more accurately directed.

Shrapnel shells, as used at the present time by the different governments, vary slightly in construction and general contour as well as in the constituents entering into their different members. As shown in Fig. 1, a completed shrapnel comprises a brass case carrying a detonating primer and the explosive charge for propelling the projectile out of the bore of the gun. The projectile itself comprises a forged shell that carries the lead bullets and bursting charge. Screwed into the front end is the combination timing and percussion fuse which can be set so as to explode the shell at any desired point and from which the flame for exploding the bursting charge is conveyed through a powder timing train and a tube filled with powder pellets down through the diaphragm to the powder pocket.

Of these members of a shrapnel, the shell and timing fuse present the most interesting features from a mechanical standpoint. The shell used by most governments is made from a forging, machined to the desired dimensions in hand and semi-automatic turret lathes as well as in ordinary engine lathes. The fuse, a complete description of which will be given later, is an extremely accurate piece of mechanism, and it is largely produced from screw machine parts, some of which, however, are forged previous to machining. The brass cartridge case—the next member of importance—is drawn up from a brass blank by successive operations in drawing presses, and is indented and headed. Following this, several machining operations on the head and primer pocket are accomplished.

Shrapnel shells are made in two distinct types, one

of which is known as the common shell, and the other as the high explosive. The common shell is a base-charged shrapnel, fitted with a combination fuse, whereas the high-explosive shell is fitted with a combination fuse and, in addition, with a high-explosive head, the head also bursting and flying into atoms upon impact. The high-explosive shell is not ruptured upon the explosion of the bursting charge in the base, but the head is forced out and the bullets are shot out of the case with an increased velocity. In the meantime, the head continues in its flight and detonates on impact. This type of shell is not used quite as extensively as the common shrapnel, and for simplicity of description the common shrapnel shell alone will be taken up in the following.

Reference to Fig. 1 will show that as far as the construction of the shrapnel shell and case is concerned, there is very little difference in those employed by the various governments. Starting with the case, it will be seen that these are almost identical, except for length and the arrangement of the head for carrying the detonating primer. There is a marked similarity in this respect between the Russian, British and German and between the American and French. The form of the explosive charge held in the brass case differs in almost every instance, but without any exception smokeless powder in some form or other is used. In the American shell, nitro-cellulose powder composed of multi-perforated cylindrical grains each 0.35 inch long and 0.195 inch diameter are used. In the Russian case, smokeless powder of crystalline structure is used. In the German, smokeless (nitro-cellulose) powder in long sticks and arranged in bundles is held in the case. The French use stick smokeless powder  $\frac{1}{2}$  millimeter (0.0195 inch) thick by 12.69 millimeters ( $\frac{1}{2}$  inch) wide. Two lengths or rows of this powder are arranged in the case. The British use a smokeless powder of crystalline structure somewhat similar to the Russian, but in

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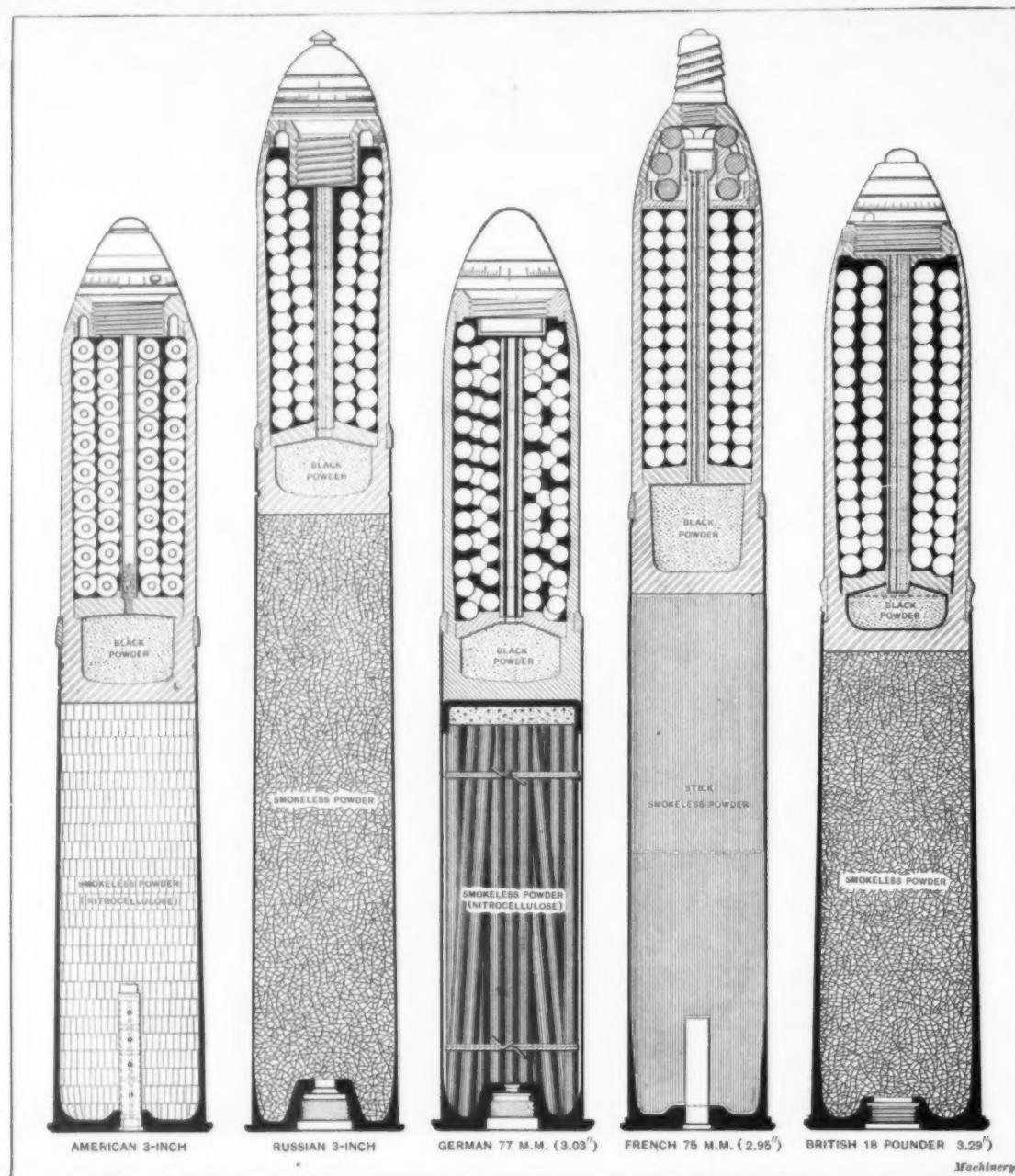


Fig. 1.—Types of shrapnel shell used by various nations.

some cases cordite has also been used, although of late this type of powder has not been quite as commonly employed.

The detonating agents or primer held in the head of the case varies in almost every type of shrapnel. Practically all primers are provided with "safety heads" so that the shrapnel can be handled without danger of premature explosion. The object, of course, of the detonating agent or primer is to send off the explosive charge in the shell for propelling the shrapnel out of the field gun.

The shell itself, as previously mentioned, is made either from a forging or from bar stock. Forgings, however, are used to a greater extent than bar stock, because the forged shell is more homogeneous in its structure than the bar stock shell, and piping—a serious objection in the bar stock shell—is entirely eliminated.

The shells used by the British, Russian, and German governments are made almost exclusively from forgings, whereas those used by the French and American are made both from forgings and bar stock. When the French shell is made from bar stock, an auxiliary base is screwed in to eliminate any danger of piping. Near the base of all shells is a groove in which a bronze or copper band is hydraulically shrunk. This is afterward machined to the desired shape and takes the rifling grooves in the gun so as to rotate the shell when it is being expelled. The body of the shell itself is slightly smaller than the bore in the gun, and the rifling band, of course, is larger and is compressed into the rifling grooves, thus rotating the projectile and keeping it in a straight line laterally during flight. The bursting charge, which in practically all cases is common black powder, is carried in the base of the shell and is usually inclosed in a tin cup. Located above this is the diaphragm which is used for carrying the lead bullets

out of the shell when the bursting charge explodes and distributes them in a fan shape. In most shells, upon exploding, the nose blows out, stripping the threads that hold the members together. It will therefore be seen that, in the explosion, the entire fuse, fuse base, tube, diaphragm, and bullets are all ejected, the shell itself acting as a secondary cannon in the air.

The range of a 3-inch shrapnel shell is about 6,500 yards, and the muzzle velocity of the quick-firing field gun ranges from 1,700 on the American to 1,930 feet per second on the Russian. The duration of flight ranges from 21 to 25 seconds. When the bullets are blown out of the shell by the bursting charge, they are given an increased velocity of from 250 to 300 feet per second. The velocity of the shrapnel at 6,500 yards is about 724 feet per second. The number of lead bullets carried in the 3-inch shrapnel shells ranges from 210 to 360. In all cases, the lead bullets are about  $\frac{1}{2}$  inch in diameter, weigh approximately 107 grains, and are kept from moving in the shell by resin or other smoke-producing matrix.

The matrix put in with the lead bullets, in addition to keeping them from rattling, is also used as a tracer. It is of importance in firing shrapnel that the position of the explosion be plainly seen. With large shells this is not difficult, but with shrapnel for field guns at long range certain conditions of the atmosphere make it difficult to see when the shell actually bursts. Various mixtures are used to overcome this difficulty. In some cases fine grained black powder is compressed in with the bullets in order to give the desired effect. In the German shrapnel a mixture of red amorphous phosphorus and fine grained powder which produces a dense white cloud of smoke is used, and in the Russian, a mixture of magnesium antimony sulphide is used.

The first fuses used in field ammunition were short iron or copper tubes filled with a slow-burning compo-

sition. These were screwed into a fuse hole provided in the shell, but there was no means for regulating the time of burning. Later—about the end of the seventeenth century—the fuse case was made of paper or wood so that by drilling a hole through into the composition the fuse could be made to burn for approximately the desired length of time before exploding the shell, or the fuse could be cut to the correct length to accomplish the same purpose.

For a considerable time all attempts to produce a percussion fuse were unsuccessful. Upon the discovery of fulminate of mercury in 1799, the chief requirement of a percussion fuse was obtained. About fifty years elapsed, however, before a satisfactory fuse was made. The first percussion fuse was known as the Pettman fuse, and comprised a roughened ball covered with detonating composition that was released upon the discharge of the gun. When the shell hit the desired object, the ball struck against the inner walls of the fuse, exploded the composition and powder charge, thus bursting the shell. There are at the present time three principal types of fuses in use: First, those depending on gas pressure in the gun setting the pellet of the fuse free—this is a base fuse; second, those relying on the shock of discharge or the rotation of the shell to set the pellet free—used in nose and base fuses; third, those depending on impact.

In shrapnel shells advantage is taken of two types of fuses, one of which is the combination timing and percussion fuse used on common shrapnel, and the other the combination timing and percussion fuse of the high-explosive type used on high-explosive shrapnel. These types of fuses are again sub-divided, but only in the manner of construction. The most common fuse is that known as the combination timing and percussion fuse of the double-banked type. This is used in practically all shrapnel fuses except the French. The advantage

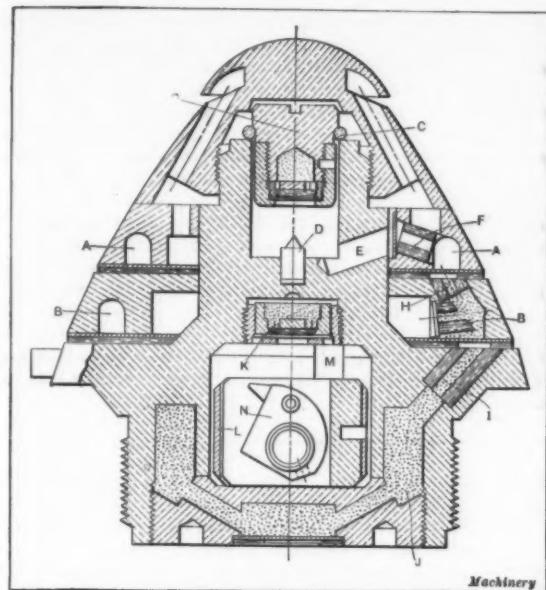


Fig. 3.—American type of confined timing and percussion fuse used on shrapnel shells.

of the double ring of composition shown at *A* and *B* in Fig. 3 is to give a greater length of composition and more accurate burning. Triple-banked and quadruple-banked fuses on the same principle have been designed, but at the present time have not been introduced.

The manner in which the combination timing and percussion fuse is regulated to discharge the bursting charge in the shrapnel shell is interesting and involves extremely difficult mathematical calculations. Before going into the method of setting the fuse, it would probably be advisable to describe briefly just how the fuse operates. As an example of the double-banked fuse, Fig. 3 shows that adopted by the American Government.

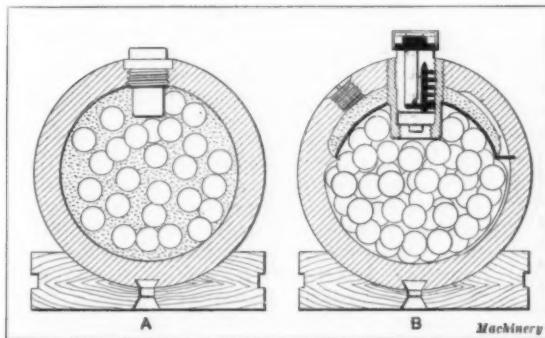


Fig. 2.—Original shell designed by Lieut. Henry Shrapnel and Col. Boxer's improvement

The following description applies to this type of fuse.

Assume first, that the timing ring is set at zero. The propelling force given to the shrapnel shell in leaving the bore of the gun is such as to sever the wire *C* from plunger *G*. Plunger *G* carries a concussion primer which is discharged by hitting firing pin *D*. The flame passes out through vent *E*, igniting the powder pellet *F* and the upper end of train *A*, and then through the vent *H*. From here, the flame is transmitted to the lower timing ring *B*, through vent *I* and the magazine *J*, and from there through the tube to the bursting charge in the base of the shrapnel shell.

Assume any other setting, say 12 seconds. The vent *H* is now changed in position with respect to vent *E* leading to the upper timing train, and the vent *I* leading to the powder magazine *J* is also changed. The flame, therefore, now passes through vent *E* and burns

vent to the powder magazine *J*. It should be understood that the annular grooves in the lower face of each timing train do not form complete circles, a solid portion being left between the grooves in the ends of each. This solid portion is used to obtain a setting at which the fuse cannot be exploded and is known as the "safety point." As shown in Fig. 6, it is marked *S* on the adjustable timing ring.

The timing fuse shown in Fig. 3 is of the combination timing and percussion type, and if the wire *C* fails to release percussion plunger *G* in Fig. 3, the shell is

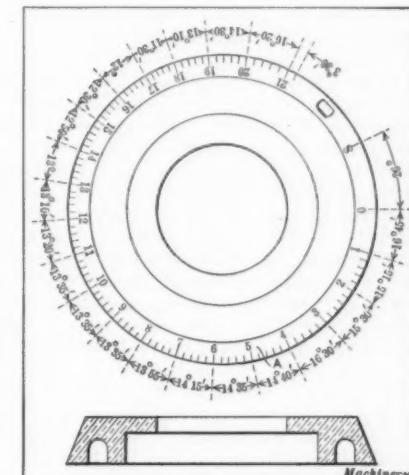


Fig. 6.—Diagram showing how timing ring on American fuse is laid out.

exploded by means of a percussion fuse which comes into use when the shell strikes. The percussive mechanism consists of a primer *K* held in an inverted position in the center of the fuse body by a cup located beneath the percussive primer. Percussion plunger *L* works in a recess in the base of the fuse body and is kept at the bottom of the recess away from contact with the primer by a light spring in plunger *M*. The firing pin *N* is mounted on a fulcrum pin, and is normally kept in the vertical position by means of two side spring plungers. When the shell strikes, the impact causes the plunger to snap up against the primer after compressing the spring in pin *M*. This causes the firing of the primer *K* and the explosive charge passes out through a hole in the percussion plunger chamber, not shown, to the magazine *J* and from there down to the powder in the base of the shell.

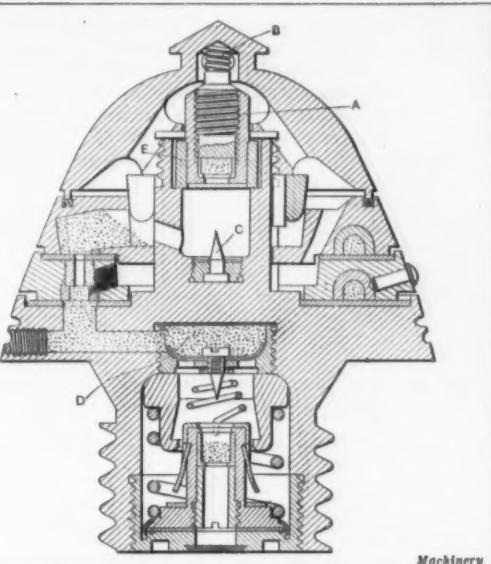


Fig. 4.—Russian type of combination timing and percussion fuse used on shrapnel shells.

The Russian fuse shown in Fig. 4 differs only in a few minor details from the American fuse the chief difference being in the arrangement of the percussive mechanism. The percussive plunger for the timing arrangement is kept up from the firing pin by means of a spring bushing *E* surrounding the body of the plunger. This bushing is expanded by the plunger which is forced through it due to the force of the shrapnel in leaving the bore of the gun. The spring *B* in the head of the fuse assists the plunger in expanding bushing *E* and in dropping down onto the firing pin *C*. The flame from the exploded primer then travels down to the powder in the shell in practically the same way that it does in the American fuse, except that the magazine chamber is located at *D* and explodes through the impact fuse chamber. The percussive arrangement for setting the shell off by impact is slightly different from that in the American fuse, in that the primer and firing pin are held apart by means of springs, the inertia of which is overcome when the shell strikes an object.

With the exception of a few minor details, the timing fuses used in American, Russian, British, German, Japanese, etc., shrapnel shells are the same. The French timing fuse, however, as shown by the diagram Fig. 5, operates on an entirely different principle. In this fuse the firing for the timing train is contained in a sealed tube of pure tin and is wound spirally around the head of the fuse. Inside of the head is the ignition arrangement. To set the timing part of this fuse, it is placed in a fuse-setting machine attached to the field gun, and by forcing down a handle on this device, a piercing point is thrust through the outer cap of the fuse, penetrating to the interior space of the head as shown at *A*. Upon the discharge of the shell from the gun, the gas pressure forces firing pin *B* back, hitting the percussive primer *C*. This causes a flame which passes out through the opening previously punched at *A* and ignites the "rope" powder fuse which is wound around the head of the fuse body. This type of fuse is also provided with a fuse which sets off the shell by impact should the timing fuse fail to work. The head of the fuse is covered with a cap with holes for the piercing point, and the whole cap can be shifted around for a short distance and set by the corrector scale marked on the body, as shown in Fig. 1. A projection on the cap engages a recess in the fuse-setting machine and provides for this movement, the machine previously being set to punch the hole.

The accuracy with which a shrapnel can be exploded in the air at any desired point is remarkable, considering the number of variable quantities that enter into the construction of the timing fuse and powder train.

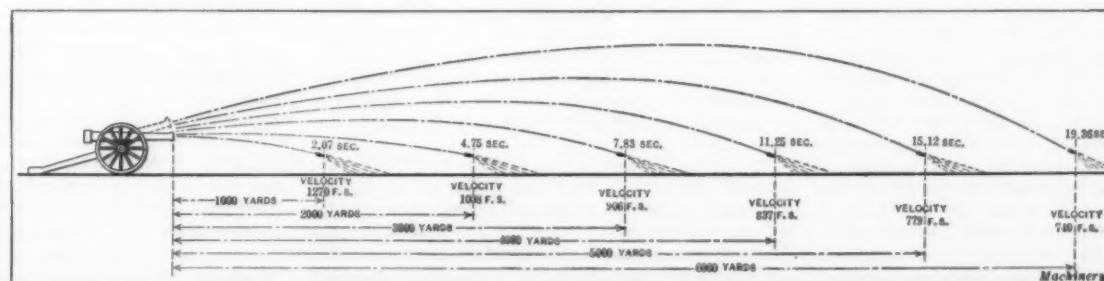


Fig. 7.—Diagram illustrating path of a shrapnel and the time of explosion at various distances.

etc. The calculations necessary for finding the correct setting on the timing ring involve the use of higher mathematics and are consequently not within the scope of this article. In the following, however, will be given a brief explanation of how a fuse is set to explode the shrapnel at a certain predetermined point.

Referring to Fig. 6, the timing ring used on the American fuse is shown. Here it will be seen that the ring is provided with twenty-one graduations corresponding to twenty-one seconds in the duration of flight of the projectile. It will also be noticed that the spacing of the graduations differs. For instance, 8 to zero, or safety to zero, occupies 26 degrees. This, as previously mentioned, is required so that the ungrooved surfaces of the timing rings can be swung around far enough to bring them in line with the vents for firing. From zero to 1 is greater than from 1 to 2. The reason for this is also in the relation of the vents. From 3 to

4 will be seen another variation. This takes into consideration the positions of the lower timing train and the trajectory of the flying missile. From 6 seconds around to 18 is practically a constant drop, taking into consideration the decrease of velocity, and from 18 on, the graduations begin to increase for two reasons: the decrease in the velocity of the missile and the action of gravity.

Diagram Fig. 7 shows in an interesting manner just how a shrapnel is fired. The range is approximately obtained by panoramic sights or other means, and a test shell fired, the point of explosion noted and the necessary corrections made. A table which has been worked out for different distances is then used. In Fig. 7 the diagram shown pertains to the American quick-firing field gun having a muzzle velocity of 1,700 feet per second and the American shrapnel of 3-inch size. It will be noted that at 3,000 yards the terminal

velocity of the shrapnel is 1,038 feet per second and the time of flight for the projectile 4.75 seconds. In other words, the timing train to explode the shrapnel at this point would be set at 4 in Fig. 6. The range of a 3-inch American shrapnel is 6,500 yards and at this point the terminal velocity is approximately 724 feet per second, the time of flight 21.92 seconds. The shrapnel, when exploded, shoots out the bullets at an increased velocity of from 250 to 300 feet per second, covering an area of about 250 by 30 yards, half the bullets falling on the first 50 yards of the beaten zone.

In manufacturing shrapnel shells a test shell is taken from every 120 and is actually fired out of a quick-firing gun into a bank of sand. If the contour of the shell in the neighborhood of the powder pocket is expanded during this test, the shell is discarded because of the liability of tearing out the rifling grooves in the gun.

### Star Clusters

OF ALL the telescopic objects in the sky none are more beautiful or more fascinating than the condensed globular star clusters. Their bewildering complexity renders them unsuitable for direct study at the telescope, but photography has now brought them within the range of systematic investigation. The technical problem which they present is by no means easy, and demands high resolving power for success.

Considerable attention was given to the star clusters by Sir John Herschel, whose attempts to depict them by hand met naturally with small success. Certain curious irregularities which he believed to exist in the distribution of the stars may be attributed to a purely subjective origin, or they may be accounted for by the absorptive influence of external dark nebulous masses. No great importance is now attached to them, and in the main the stars may be considered as distributed with radial symmetry. But one curious feature noticed by Sir John Herschel has been confirmed by later study. The stars in a cluster tend to divide into two classes of magnitude, a brighter and a fainter, separated by a distinct interval. Can this be a visible division of stars presumably at the same distance and of nearly equal age into the two classes of giant and dwarf stars inferred by Hertzsprung and H. N. Russell?

About 20 years ago Prof. S. I. Bailey, at that time at Arequipa, devoted considerable study to photographs of the chief globular clusters. His work proceeded on two lines. On one hand he made systematic counts of the stars recorded, thus laying the foundation for statistical investigations of their arrangement in space. And on the other he investigated the magnitudes of the stars, and was thus led to the remarkable discovery that several clusters contain a high proportion of variable stars, a ratio of 1 to 7 in the extreme case of M3. His detailed results for the clusters  $\omega$  Centauri and M3 have been published in two beautiful memoirs. The type of variation is of a distinct character, though a few isolated examples have been found elsewhere in the sky, with a period of about 12 hours and a rapid rise to maximum. In the case of M3 the variation is singularly true to one type, the range between maximum and minimum being two photographic magnitudes. Some clusters, notably M13, are almost entirely devoid of such variables; where they do occur they are apparently confined to the stars of the brighter order of magnitude.

The question of the distribution of stars in clusters was discussed by Prof. E. C. Pickering. Using counts on the clusters  $\omega$  Centauri, 47 Tucanae and M13 (Herculis), he formed the important conclusions: (1) that the law of distribution is essentially the same for different clusters, (2) that the bright stars and the faint stars of a cluster obey the same law. He represented graphically the curve of apparent (projected) density for different distances from the center, and attempted without success to reproduce it by assuming laws of the form  $1/r^2$  and  $(1-r)^n$  for the density in space. The latter form was also tested by Mr. W. E. Plummer with much the same result on an extensive series of measures of the stars in M13.

The next important contribution to the subject is due to H. v. Zeipel, who measured the positions of the stars in M3 (Can. Ven.). By adapting the solution of a certain integral equation studied by Abel he showed how the law of distribution in space may be deduced numerically from the observed distribution as it is seen in projection. Later he compared the law of density in space arrived at in this way with that which obtains in a gravitating spherical mass of gas in isothermal equilibrium. The result represents the density of the cluster satisfactorily near the center, but in the outer regions the cluster is less dense than the theory requires.

The physical conception thus introduced suggested other possibilities. A sphere of gas in adiabatic, instead of isothermal, equilibrium might be chosen as the standard of comparison. A series of states exists, depending on the constant ratio  $\gamma$  of the specific heats of the gas,

which have been extensively studied by Lord Kelvin and others. Emden's "Gaskugeln" is a work dealing exhaustively with the subject. In general, the law of density cannot be expressed in finite terms. But there are exceptional cases in which the differential equation possesses a very simple solution. One of these, discovered by Schuster, corresponds to the value  $\gamma=1.2$ . Here the law expressing the density at the distance  $r$  from the center takes the form:

$$3a^4N/4\pi(a^4+r^4)^{3/2},$$

where  $N$  is the total mass or number of stars. This is finite, although the distribution extends to infinity. If a finite boundary be expected it is impossible to fix one by the counts, and attempts to do so have been proved illusory by the occurrence of characteristic variable stars beyond the supposed limit. However this may be, a comparison of the law with Bailey's counts of the  $\omega$  Centauri cluster showed immediately an agreement within the limits within which radial symmetry is observed. I next compared the law with Pickering's curve of the projected densities, based on the clusters  $\omega$  Centauri, M13 and 47 Tucanae (bright and faint stars treated separately). The accordance was again excellent, and left little doubt that the law represented much more than a mere formula of interpolation. When, however, v. Zeipel's counts of M3 were examined, the outer region was found to conform with the law, while the inner revealed a higher density than was to be expected. As v. Zeipel had, on the other hand, succeeded in representing the central distribution by the isothermal law, it was suggested that the true standard of comparison was a central isothermal core surrounded by an adiabatic envelope, a composite state of equilibrium actually contemplated by writers in the thermodynamics of the subject. Afterwards, by the use of similar methods, Prof. Strömgren proved that M5 (Serpentis) possesses a structure which, whatever the cause, is identical with that of M3. V. Zeipel remarked that the excessive central condensation was more marked among the bright than among the faint stars.

The problem has again been discussed by v. Zeipel in an elaborate memoir, using in this instance counts of the stars in M2 (Aquarii), M3, M13 and M15 (Pegasi). He first finds solutions corresponding to these values of  $\gamma$ :

$$(M2) 1.200, (M3) 1.156, (M13) 1.183, (M15) 1.179$$

Thus M2 conforms with the same simple law, which I had found to hold so perfectly for  $\omega$  Centauri. On the other hand, M3 is again seen to depart from it, and even with the new value of  $\gamma$  the representation is far from good. The law of density here contemplated is a solution of the equation:

$$\frac{d^2(r\rho^{\gamma-1})}{dr^2} + r\rho = 0,$$

and satisfies a physical condition in being regular at the center. The general solution, however, possesses a singularity at this point, and contains an additional arbitrary constant. Thus the particular law given above is only a special case of the general solution for  $\gamma=1.2$ , which, as v. Zeipel shows, can be expressed in elliptic functions. Accordingly, he abandons the central condition, and introduces the additional constant which is to be determined, together with  $\gamma$ , for each case. With this modification of the theory the values of  $\gamma$  became:

$$(M2) 1.194, (M3) 1.198, (M13) 1.203, (M15) 1.197,$$

so that within the limits of uncertainty in every case the distribution of stars is consistent with a solution of the above differential equation when  $\gamma$  is assigned the value 1.2.

The analogy between the distribution of stars in a condensed cluster and the density in a spherical mass of gas of a particular type in adiabatic equilibrium thus seems to be fairly established. Even if it be supposed that the cluster is the outcome of an original nebula the question still remains why the distribution of matter should persist long after its condition has completely changed, or why the arrangement should resemble what might be expected of certain vapors (e.g., chloroform). The answer

given by v. Zeipel on the basis of a strict mathematical analysis is that this is in conformity with a kinetic theory which applies to an aggregate containing a high proportion of Keplerian binaries. This may be a bold application of the law of large numbers, but it is certainly an interesting conception. Since there is every reason to believe that all short period variables are binary systems the observed occurrences of these in clusters lends support to the view, though they can only represent the exceptionally close systems. The investigations here described refer exclusively to the highly condensed clusters. But there exist also clusters showing states of concentration in varying degree until probably all visible trace of organic connection is lost. In Strömgren's view the whole series represents an order of evolution by which the dense clusters grow out of more scattered forms. Whether the results will throw light on the wider problems of the structure of the sidereal universe seems doubtful in view of certain conclusions drawn by Poincaré, Jeans and Eddington as to the relevance of the kinetic theory. But taken by themselves they present questions of the highest interest which are likely to repay further study.—H. C. PLUMMER in *Nature*.

### Fixation of Atmospheric Nitrogen

EXPERIMENTS have been conducted by I. A. Stahler and J. J. Elbert, as reported in the *Ber. Deut. Chem. Ges.*, 46, p. 2060, for obtaining boron nitride; and as most naturally occurring compounds of boron are combined with oxygen, the first step was to ascertain the best methods for their reduction, followed by the combination of the boron obtained with nitrogen. The reduction of boron trioxide by carbon begins to take place at 1,200 degrees; in the presence of nitrogen, calcium borate (borocalcite) undergoes reduction at 1,280 degrees, reaction probably taking place according to the equation:  $\text{CaB}_2\text{O}_4 + 8\text{C} + 3\text{N}_2 = 4\text{BN} + \text{CaCN}_2 + 7\text{CO}$ .

The electrolysis of molten borax gave yields of boron to the extent of 12.1 per cent. Carbon electrodes were first used, but they broke off repeatedly at the surface of the fusion; iron electrodes lasted longer, but they also broke off after a time. Attempts to reduce boron trioxide by means of calcium carbide at 1,625 degrees made it probable that the product of reaction was calcium boride, which has previously been prepared by Moissan.

Before carrying out further experiments on the production of boron nitride it was necessary to determine its stability; it was found that decomposition with evolution of nitrogen only commenced to take place at 2,450 degrees; this temperature of decomposition holds only in the presence of carbon, since the boron nitride was contained in a graphite crucible.

The next experiments were confined to mixtures of carbon with either boron trioxide or borocalcite. These were heated to different temperatures in an atmosphere of nitrogen under different pressures, a special electrical furnace having been constructed in which reactions could be carried out at pressures up to 500 kilogrammes per square centimeter, and at temperatures up to 2,500 degrees. With mixtures of boron trioxide and carbon and nitrogen at atmospheric pressure, the best yield, 26.28 per cent of boron nitride, is obtained between 1,500 degrees and 1,700 degrees. With increasing pressure the yield increases, more than 85 per cent of boron nitride being obtained at a pressure of 70 kilogrammes per square centimeter and a temperature of 1,600 deg. When the boron trioxide is replaced by borocalcite, a nearly theoretical yield of boron nitride, according to the equation given above, is obtained when the temperature is maintained at 1,850 degrees for 30 minutes and 1,400 degrees in 15 minutes; increase in pressure of the nitrogen has no effect on the yield. At normal pressures the amount of nitrogen absorbed per gramme of boron is much greater with borocalcite than with boron trioxide; only at very high pressures are better results obtained with boron trioxide than with borocalcite.

# The Chemical Industries of Germany—I\*

## An Historical Review of Processes and Conditions

By Prof. Percy F. Frankland, F.R.S.

It is remarkable that the Royal House of Prussia has during many centuries been associated in one way or another with chemical enterprises of various kinds. Thus already the second ruler of the country, the Markgraf John (1608-1619) was actually surnamed "the Alchemist" in consequence of the zeal with which during many years he pursued his investigations on the transmutation of metals, while a number of his successors exhibited great interest in the same problem—the manufacture of gold—which has never failed to fascinate the needy princes—and what princes are not needy?—of all ages and all nations.

The Great Elector (1640-1688), who did so much to advance the power of Prussia, was a patron of chemistry, which was just then beginning to emerge, as an experimental science from the obscurantism of alchemy. He provided the celebrated Kunkel with a laboratory and glass furnaces on an island in his park at Potsdam, and it was there then in 1678 Kunkel made the discovery of ruby glass, produced by means of traces of gold, and which is still an unsurpassed method of coloring glass for ornamental purposes. Kunkel also rediscovered phosphorus, which has previously, in 1669, been obtained by the alchemist Brand of Hamburg, who had quite accidentally produced it in the course of his attempts to extract the Philosopher's Stone out of urine.

But while the discovery of yellow phosphorus is thus of German origin, its production on an industrial scale was, until twenty years ago, only carried on in England and France. In 1892, the manufacture of phosphorus by electrothermic means was introduced into Germany by the Chem. Fab. Griesheim-Elektron at Frankfort. Red phosphorus was discovered by Schröter, an Austrian chemist, in 1848, and was adapted for safety-matches by the German Böttger in the same year. His invention was first taken up in Sweden, and was not adopted until ten years later in Germany.

The match industry has assumed its largest dimensions in Germany. Thus the German annual production in 1912 was \$23,000,000.<sup>2</sup> The value of all matches (British and foreign) consumed in Great Britain in 1910 is estimated at \$6,468,750—about nine matches per day per head. Messrs. Bryant and May's (by far the largest English concern) turned out 1,152,000,000 boxes in 1907. This represents about one half the British output. In 1907 the total value of British production was \$3,875,000, of which \$380,000 worth was exported.<sup>3</sup> The British export of matches is diminishing. It is worthy of note that Japan in 1901 exported matches to the value of \$6,000,000.

### PORCELAIN.

Another great German industry owes its origin to alchemistic studies made by Böttger in the reign following that of the great Elector, namely, that of Frederick III. (1688-1713), first King of Prussia. Having succeeded in making gold before witnesses, Böttger was seized by order of the Elector of Saxony and was "interned" at Dresden, where, although he did not succeed in making the much-desired gold, he founded along with the physicist Tschirnhaus, the celebrated Dresden porcelain industry.

The astute Frederick the Great (1740-1786) was anxious to manufacture the Dresden ware at Berlin and to this end commissioned his court apothecary, Johann Heinrich Pott, to institute investigations. These attempts were, however, all unsuccessful.

The great Frederick placed much faith in secret agents and it was by means of spies that he succeeded in discovering the secrets of the Dresden porcelain manufacture, for at his instigation an enterprising merchant, bearing the name of Gotzkowski, with the assistance of a Saxon workman, brought the secrets of the Dresden process to Berlin and established a porcelain factory in the Leipziger Strasse, which still remains the warehouse for the Berlin porcelain goods. But Frederick later stopped the pecuniary assistance with which the factory had been subsidized, and Gotzkowski was forced to sell the concern of Frederick for about \$150,000, and so was established the celebrated Berlin Royal Porcelain Factory, among the products

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<sup>1</sup>The author has much pleasure in acknowledging the assistance he has received from the valuable compilation by Prof. Lepsius of Berlin, "Deutschlands Chem. Industrie 1888-1913," and from that by Dr. Duisberg, of Elberfeld, "Wissenschaft und Technik," 1911.

<sup>2</sup>Molinari, "General and Industrial Inorganic Chemistry," 1912.

<sup>3</sup>Clayton.

of which are the well-known crucibles and evaporating basins. The flourishing state of the German porcelain and pottery manufacture is attested by the fact that during the past twenty-five years the number of works has increased from 228 to 359, and the number of workpeople employed from 37,000 to 66,000. In 1912 the German export of china, earthen and stoneware were valued at upwards of \$17,500,000.

### GLASS.

Even still more important is Germany's glass manufacture, for which she has long been pre-eminent. The annual export in recent years has been over \$35,000,000.

### CYANIDE INDUSTRY.

In the early eighteenth century an accidental discovery was made by Diesbach, a Berlin color-maker, which has proved of great industrial importance. Diesbach was preparing what is known as Florentine lake, a red pigment obtained by precipitating a solution containing cochineal extract and an iron salt with caustic potash. It so happened, however, that the potash used by Diesbach had been in contact with bone oil containing some cyanide, and the result was that, instead of the result he anticipated, a magnificent blue coloring matter was obtained. This substance, which is still known as Berlin or Prussian blue, was the first cyanogen compound to be discovered.

The cyanogen compounds have played a most conspicuous part in the development of organic chemistry, and every source of cyanogen has been exploited for obtaining them. In recent years the demand has increased enormously owing to the employment of sodium and potassium cyanides in the extraction of gold. To meet this demand a number of synthetical methods for their preparation have been super-added.

Germany's annual production of cyanides is estimated at 10,000 tons, valued at \$3,250,000, or about half of the world's production.

### BEET-SUGAR INDUSTRY.

Another industry also had its beginnings in the eighteenth century during the reign of the Great Frederick, and was the outcome of the laborious researches of Marggraf (born in Berlin in 1700, and a pupil of Stahl) on the occurrence of sugar in the vegetable kingdom. Of the numerous plants investigated from this point of view he found that the beetroot (*Beta vulgaris*) contained the largest proportion of saccharine material and that the sweet-tasting substance was identical with that present in the tropical sugar cane (*Saccharum officinarum*).

It was not, however, until some fifty years later that the observations of Marggraf led to the first beet-sugar factory in the hands of Franz Karl Arched, who was subsidized in this venture by the Prussian King, Frederick William III. (reign 1779-1840), who was also the founder of the University of Berlin.<sup>4</sup>

The beet-sugar industry had to contend with strenuous competition by the cane-sugar manufacturers. The industry was, however, greatly promoted when, in 1806, Napoleon issued his famous edict closing the European ports to British goods. The vast extent of this industry can be gathered from the following figures:

Total sugar crop for 1912-13: Cane sugar, 9,211,755 tons; beet sugar, European (one third German), 8,310,000 tons; beet sugar, United States, 624,064 tons; total, 18,145,819 tons.

The sugar industry should give us food for serious reflection when we consider the following facts: United Kingdom spends annually \$115,000,000 on 1,700,000 tons imported sugar. Germany produces \$180,000,000 worth of beet sugar on 1,300,000 acres. France produces \$65,000,000 on 570,000 acres; all continental countries together produce \$580,000,000 on 6,000,000 acres.<sup>5</sup> In the United Kingdom there is only one small experimental beet-sugar factory in existence. The beet-sugar industry is of particular interest in connection with the present European crisis, inasmuch as it is a most notable example of an industry which largely owes its successful inception to a state of war which disturbed the previously established order of things in the matter of sugar supply.

In this country (Great Britain) agriculture is well

<sup>4</sup>There was no University in Berlin until 1809, but the following figures will show how Prussia has made up for lost time in this respect. In 1913-14, there were 7,613 male and 770 female matriculated students, and 4,113 male and 89 female non-matriculated students. The annual income was \$1,231,550, of which \$1,023,250 came from the state, \$204,500 from fees, etc., and \$8,300 from other sources. The annual expenditure was \$1,231,550, of which the teaching staff accounted for \$523,950; departmental expenses, \$500,700; building expenses, \$53,050; reserve, \$33,400; administration, bursaries, etc., \$120,450. ("Minerva," 1914.)

<sup>5</sup>C. W. Fielding, *Morning Post*, January 23d, 1915.

known to be productive of a conservative frame of mind, but that it is not so in Germany is well illustrated by the extraordinary progress which has been made in the cultivation of the sugar beet under the guidance of systematic scientific research. Thus, in 1840, 100 kilogrammes of beet gave 5.9 kilogrammes of sugar; in 1850, 7.3; in 1870, 8.4; in 1890, 12.5; and in 1910, 15.8. In 1871 the mean production of beet per hectare<sup>6</sup> was 24 quintals,<sup>7</sup> and in 1910, 300 quintals. In 1867 the consumption of coal for 100 kilogrammes of beet was 35 kilogrammes; in 1877, 24; in 1890, 10, and in 1900, 7. Further economy in coal has been affected by means of the Kestener concentrator.<sup>8</sup>

### SULPHURIC ACID, SODA AND BLEACHING POWDER.

Sulphuric acid was discovered by the German alchemist Basil Valentine in the fifteenth century. The production of this fundamental acid, however, on any considerable scale took its origin in Birmingham, where Dr. Roebuck in 1746 introduced the classical leaden chamber process. At the beginning of the nineteenth century it became an industry of great importance, more especially in England, because of this acid being required for the manufacture of carbonate of soda by the Le Blanc process.

The manufacture of Le Blanc soda was taken up in England in 1814, especially in connection with soap-making, and it was in England that this manufacture assumed the largest proportions. The enormous advances made in this manufacture during the past century may be gathered from the fact that the price of carbonate of soda in 1818 was about \$210 per ton, while to-day it is only about one tenth of that amount. One of the determining factors which made England the principal home of soda manufacture was the great development of the English cotton industry during the nineteenth century.

During a large part of the last century England manufactured Le Blanc soda, sulphuric acid and bleaching powder<sup>9</sup> for most of the world. But during the latter half of the century the rival ammonia soda process made its appearance. The original discovery of the reaction on which it depends—it was first patented in England by Dyas and Hemming in 1838—is ascribed to several different persons, but the process was first made an industrial success in Belgium by M. Ernest Solvay. The Couillet works were founded with a capital of about \$30,000 in 1863; the numerous affiliated works are now to be found in Belgium, England (Brunner, Mond and Company), Germany, France, Italy, Spain, Austria-Hungary, Russia and North America. They employ 35,000 persons. During the fifty years the price of soda had been reduced from \$80 to \$20 per ton. The displacement of Le Blanc soda by ammonia-soda involved the introduction of new methods of chlorine manufacture. After numerous abortive attempts in various directions, the successful production of electrolytic chlorine has been achieved, and about half of the bleaching powder in the world is now made by this means.

Electrolytic chlorine is now often converted into liquid chlorine (12 cents a kilogramme), of which large quantities are used at Stassfurth for the annual preparation of 500,000 kilogrammes of bromide, and the Badische Aniline und Soda Fabrik used in 1900 more than 1,000,000 kilogrammes for the preparation of chloroacetic acid employed in the manufacture of synthetic indigo.

In the manufacture of sulphuric acid, again, the old-fashioned English or leaden chamber process has not been allowed to remain unchallenged, for since the beginning of the present century it has had to meet the competition of the so-called contact process. This is based on a long known reaction,<sup>10</sup> which, however, remained almost unutilized until the meticulous industry of German chemists and the courageous enterprise of German manufacturers developed it into a commercially successful process, which was elaborated in the works of the Badische Aniline und Soda Fabrik.

The ammonia-soda and the contact sulphuric acid<sup>11</sup> processes, although carried out in England, have been largely instrumental in making other countries, more especially Germany and the United States, independent of the English production of these all-important chemicals.

<sup>6</sup>Hectare = 2.5 acres.

<sup>7</sup>Quintal = 100 kilogrammes.

<sup>8</sup>Molinari, "General and Industrial Org. Chem.," 1913.

<sup>9</sup>Discovered by Tennant in 1799.

<sup>10</sup>This reaction had for many years been used by Messel in England, but only for the manufacture of So<sub>2</sub>.

<sup>11</sup>The Clayton Aniline Company and Nobel's Explosive Works have contact sulphuric acid plant.

In 1882 the world's consumption of soda was 700,000 tons (160,000 ammonia-soda), and in 1902, 1,760,000 tons (250,000 Le Blanc). In England, in 1876, \$35,000,000 was invested in the industry, which gave employment to 22,000 workpeople. In 1880 the British output was 430,000 tons, and in 1896 it was 800,000 tons. North America in 1886 produced 1,100 tons, and 300,000 tons in 1898; and Germany in 1878 made 42,000 tons, 300,000 tons in 1901 and 400,000 tons in 1910.<sup>12</sup> The first soda works in Germany was only erected in 1843 by Hermann at Schönebeck, near Magdeburg, and the first chamber by Kunheim in 1844 on the Tempelhof Plain near Berlin. (See also the statistics in Table I).

#### HYDROGEN INDUSTRY.

The electrolytic production of soda and chlorine is, of course, attended with the evolution of enormous volumes of hydrogen. At first this gas was allowed to go to waste, but gradually interesting and important uses have been found for it.

1. Dirigible balloons have been rendered possible by taking advantage of the lightness of the internal combustion engine. One horse-power engines are but little heavier than 1 kilogramme. Twenty-seven thousand cubic meters of hydrogen is required for a modern airship. The balloon sheds are often established near electrolytic soda works, or the gas may be transported in steel cylinders compressed to 150 atmospheres. Five hundred cylinders containing 2,750 cubic meters of gas are placed on one railway wagon and more than eight such loads are required for the filling of a single Zeppelin.

2. Autogenous welding with oxyhydrogen flame, a most important application of hydrogen, was introduced at the beginning of this century by the Chemische Fabrik Griesheim-Elektron. The oxy-acetylene flame is now more commonly used.

3. Artificial gems are made by means of oxy-hydrogen flame. Some thirty years ago C. V. Boys succeeded in fusing quartz with the oxyhydrogen flame and then drawing it out into incredibly thin fibers, which have proved of the highest value for certain physical experiments of extraordinary delicacy. The same source of heat was much later, in the nineties, employed by the French investigator, Michaud, to reconstruct rubies from small fragments of this gem. At the beginning of this century Verneuil and Paquier, in Paris, succeeded in making synthetic rubies. A little later Wild, Miethe and Lehmann in Germany elaborated methods for producing synthetic corundum, rubies, amethysts and sapphires, which are manufactured by the Elektro-chemische Werke at Bitterfeld. These products are identical in chemical composition and physical properties with the natural gems, and the rarest varieties of these can be obtained at will. Fused alumina (very pure) gives corundum; fused alumina + 2½ per cent chrome oxide gives ruby; fused alumina + magnesia and titanium oxide and ferric oxide gives blue sapphire. These synthetic gems are now manufactured to the extent of about 6,000,000 carats annually (1 carat = 0.205 gramme), or 1,230 kilograms or more than 1 ton. Experienced connoisseurs can, however, distinguish between the natural and artificial gems, with the result that the former have not diminished in value. Natural rubies or sapphires of 2-4 carats cost \$100 to \$250, and larger stones up to \$750, while the artificial would only cost 1/500 to 1/1000 of those amounts.

A still more recent and much more important application of hydrogen is for the hardening of fats, which depends on the transformation of unsaturated into saturated acids by means of hydrogen in the presence of a catalyst (nickel, palladium, etc.).

#### INDUSTRIES CONNECTED WITH ARTIFICIAL ILLUMINATION.

The world is greatly indebted to Germany for inventions which have largely revolutionized artificial illumination, firstly, in connection with gas and more recently in respect of electric lighting.

Thus, one of the most remarkable discoveries in this domain was that of incandescent gas lighting, which was made by the Austrian Count, Dr. Carl Auer v. Welsbach of Rastersfeld in Styria, as the result of lengthy, laborious and ingenious researches. The now so familiar gas-mantles are prepared by the ignition on the cotton frame of a mixture of 99 per cent of thorium nitrate and 1 per cent of cerium nitrate.

The source of these rare earths is monazite sand, the elaboration of which has become a very important industry depending on fractional crystallization, which already many years ago was brought to such a high pitch of perfection in the laboratory of Sir William Crookes. Out of this monazite sand Hahn in 1910 succeeded in extracting mesothorium and the process is carried out on a large scale at the works of Dr. O. Knöfler and Company at Plötzensee near Berlin. Radium bromide is worth about \$85 a milligramme, mesothorium about \$37.50 a milligramme. The mesothorium is only present in the monazite sand in extremely small proportion, about one part in 150,000,000.

I may also refer to Auer-metal, a preparation of iron (Fe 30 per cent) containing cerium, which sparks when

scratched with hard steel, and which is familiar as a substitute for matches.

Another outlet for the use of hydrogen has been in reducing the rare metals osmium (melting point 2,500 deg. Cent.), tantalum (melting point 2,300 deg. Cent.) and tungsten (melting point 2,850 deg. Cent.).

In 1903 the Auer Company showed that the carbon filament of electric incandescent lamps could be replaced by an osmium filament, with an economy of 50 to 60 per cent of current. In 1905, Siemens und Halske showed that a tantalum filament was cheaper and more

of nitrogen at all, man had solved empirically by growing leguminous plants in the rotation of his crops, thereby increasing the fertility of the soil, although the mechanism of this time-honored procedure was only experimentally demonstrated in the last decades of the nineteenth century by the German investigators, Willfahrt, Hellriegel and Nobbe.

#### FIXATION OF ATMOSPHERIC NITROGEN BY INORGANIC MEANS.

1. This has been successfully accomplished by the Birkeland and Eyde electric furnace, and the Schönerr

TABLE I—PRODUCTION IN TONS, 1910\*

	Germany	England	France	United States	Europe	World
Sulphuric acid (H <sub>2</sub> SO <sub>4</sub> )	1,250,000	1,000,000	500,000	1,200,000	3,700,000	5,000,000
(of this by contact process)	400,000	—	—	250,000	—	—
Soda	400,000	700,000	200,000	250,000	—	2,000,000
(of this Le Blanc soda)	30,000	120,000	—	—	—	150,000
Saltpeter consumption	786,000	93,000	337,000	523,000	1,740,000	2,360,000
(of this for nitric acid)	150,000	—	—	50,000	—	—
Hydrochloric acid (30 per cent)	450,000	—	—	—	—	300,000
Bleaching powder	100,000	—	—	—	—	150,000
(of this electrolytic)	70,000	—	—	—	—	—

\*Dulberg, "Wissenschaft und Technik," 1911.

\*\*Already in 1805 the estimated production of hydrochloric acid in England was 1 million tons, and for the whole of Europe 2 million tons (Mollnari).

advantageous, and in 1906 that the tungsten filament was even still better. Tungsten occurs in sufficient quantity in nature as wolframite (iron tungstate) and scheelite (calcium tungstate) to enable the metal to be now sold as filament-metal for \$1.50 to \$1.75 a kilogramme.

Some idea of the enormous and increasing scale on which the incandescent lamp manufacture is carried on in Germany may be gathered from the figures in Table II.

TABLE II—PRODUCTION IN GERMANY.

	1911	1912
Metallic-filament electric lamps	47,211,892 pieces	76,185,721 pieces
Carbon-filament electric lamps	24,791,196 pieces	20,975,348 pieces
Incandescent gas mantles	126,050,954 pieces	135,320,173 pieces
Arc-lamp carbons	10,740,025 kilos	11,093,154 kilos

According to V. B. Lewes, the consumption of gas-mantles in 1912 was: Germany, 100,000,000; America, 60,000,000; England, 38,000,000; France, 16,000,000; Belgium, 3,500,000; Italy, 3,000,000; Russia, 1,500,000.

The special tax imposed in Germany on lighting apparatus realized from the above sources in 1912 was \$4,000,000.

#### AMMONIA.

Of the commoner inorganic chemicals which are produced on the largest scale, one of the most important is ammonia, which has for many years been obtained as a by-product in the manufacture of coal gas.

So backward was this industry in Germany, that actually even as late as 1874 the ammoniacal liquor from their gas works was run to waste. All the more remarkable is the state of affairs to-day as betrayed by the following figures. The world production of ammonium sulphate was 210,000 tons in 1890, 500,000 tons in 1900, and 1,330,000 tons in 1912. Germany's production of ammonium sulphate in 1912 was about 370,000 tons.

The principal use of sulphate of ammonia is as a nitrogenous fertilizer, as which it competes with Chili saltpeter; they may be taken as of equal money value per unit of nitrogen. In this connection Germany's manure bill, given in Table III, is interesting.

TABLE III—GERMANY'S MANURE CONSUMPTION.

	1888	1912
	Tons	Tons
Chili saltpeter*	225,000	650,000
Sulphate of ammonia	50,000	500,000
Superphosphate	250,000	1,800,000
Basic slag	250,000	2,200,000
Crude potash salts	160,000	3,000,000
Lime	—	800,000
Other manures	500,000	500,000
Total value		\$150,000,000

\*The total import of Chili saltpeter into Germany in 1912 was 800,000 tons, of which only 150,000 tons was used for manufacture of potassium nitrate and nitric acid.

It is the ambition of the Germans, firstly, to make themselves independent of the industrial products of other countries, and secondly, to produce in excess of their own needs and to impose this surplus on the rest of the world. Thus, they pride themselves on displacing more and more of the foreign Chili saltpeter by home-made sulphate of ammonia, and in 1911 they used in agriculture 75,000 tons of ammoniacal nitrogen against 70,400 tons of foreign saltpeter-nitrogen. This partial success they look forward to making complete and decisive by developing new methods of producing ammoniacal nitrogen and nitrates.

Of such methods there are already two in operation, and they are associated with that great problem which confronts mankind as a whole. How to supply the combined nitrogen, which will be necessary to build up the food-stuffs for the teeming millions of the future, after the deposits of Chili saltpeter are exhausted? This is the same problem as that of fixing the nitrogen of the air, which long ago, before anything was known

electric furnace of the Badische Anilin und Soda Fabrik. These are simply realizations on the industrial scale of laboratory experiments made by Cavendish 130 years previously. This method is applicable only in Norway or other countries where abundance of water power renders the production of cheap electrical energy possible. It is being carried on by an international company at Notodden in Norway. They propose to use 300,000 horse-power capable of yielding 150,000 tons lime-saltpeter (15.20 per cent N) or about one twelfth of the total amount of Chili saltpeter used by the world. Germany possesses but little water-power so that this process is of only indirect interest in connection with German chemical industry.

2. Nitrogen may also be fixed by calcium carbide at high temperatures. This discovery was made by the German chemists Frank and Caro. \$25,000,000 capital is already embarked in this industry by various companies of Europe and America. About 120,000 tons is produced annually, about one quarter of which in Germany. The crude calcium cyanamide (about 20 per cent N) may be used directly as a nitrogenous manure or may be made to yield ammonia. The production of calcium carbide involves the use of electric furnace and hence cannot be carried on economically on a very large scale in Germany owing to the limited water-power.

3. Nitrogen and hydrogen may be combined at higher temperature and especially under high pressure. The long known fact that the reaction, N<sub>2</sub> + 3H<sub>2</sub> = 2NH<sub>3</sub> is realized to a very small extent at high temperatures has been investigated in recent years by Haber and Le Rossignol at Karlsruhe, and, guided by the principles of modern physical chemistry, Haber has elaborated, after overcoming extraordinary technical difficulties, an industrial process which promises to be of great importance in the future. The most advantageous conditions were to be found: Pressure, 200 atmospheres; temperature, 500 deg. Cent.; catalytic agent, osmium, uranium, etc.

Production of ammonia by the Haber process has been carried out on a commercial scale by the Badische Anilin Company since the summer of 1913, and a plant capable of yielding 130,000 tons of sulphate of ammonia per annum was to have been ready during the present year. Inasmuch as the German Color Syndicates have severed their connection with the Norwegian niter undertaking, it would appear that they regard the Haber ammonia process as being more likely to be capable of capturing the inorganic nitrogen market of the world.

This synthetic production of ammonia obviously involves cheap hydrogen. I have already referred to electrolytic hydrogen, but there are cheaper sources. Thus water-gas contains theoretically equal volumes of hydrogen and carbon monoxide; the carbon monoxide (boiling point—192 deg. Cent.) can be removed by liquefaction from the hydrogen (boiling point—253 deg. Cent.) Similarly the nitrogen required for the process is obtained from the fractional distillation of liquid air. The synthesis of ammonia thus dovetails with the possibilities of cheap low-temperature production for which the world is so largely indebted to the German engineer Carl von Linde of Munich.

The German ambition to make their combined nitrogen at home does not stop at the production of synthetic ammonia, for there are still large requirements in respect of nitrates (Germany produces upward of \$7,500,000 of nitric acid annually from Chili saltpeter) which have to be satisfied from foreign sources. They hope, however, to fill this gap in the home-production of combined nitrogen by utilizing a reaction discovered by Kuhlmann<sup>13</sup> as long ago as 1839, in which ammonia and air burn to nitric acid in the presence of platinum as a catalytic agent.

(To be continued)

# The Earth Considered as a Heat Engine\*

## A Chapter in the Thermodynamics of Nature

By George F. Becker, United States Geological Survey

IMAGINE that the earth solidified in such a way that fluid equilibrium were perfectly preserved and that the exterior were perfectly smooth, presenting an ideal equipotential surface of uniform temperature. Suppose that the only differences between different portions of this surface were in the diffusivity (that there are large variations in the diffusivities of different rocks, the published determinations clearly show). For simplicity's sake, suppose that a certain square area had a uniform diffusivity smaller than that of the surrounding surface. It is evident that this square would cool more slowly than the adjacent portions, and by reason of the slower escape of heat it would develop a slight relative elevation—provided indeed that the material of the globe contracted in cooling as almost all substances actually do. Furthermore, the relative contraction of the surrounding mass would bring to bear a pressure on all four sides of the square, and this pressure would extend downward as far as the difference of temperature was sensible. Such a pressure might even suffice to rupture the rock within the square.

Thus a difference in diffusivity would bring about an intumescence on the surface of the globe followed by the formation of four systems of joints, which, in the simple case supposed, would cross one another at right angles at the surface, and dip at about 45 degrees in four directions.<sup>1</sup> These joints are equivalent in voids, which as I have recently shown may, in extreme cases, approach 6.73 per cent of the volume.<sup>2</sup> Thus a further very considerable intumescence or uplift would result, and an additional diminution in the diffusivity, because joints interfere with the conduction of heat. This diminution would further increase the depth to which sensible differences in temperature on the same horizontal plane would extend. Besides systematic rupture it is evident that the lateral pressures on the square column would, or might, bring about deformations and the crumpling of layers originally plane.

It would seem then that the initial difference in diffusivity need not be great eventually to ensure a considerable uplift within the hypothetical square, since so soon as it sufficed to establish a temperature difference of a few degrees, the process of uplift would be increased by the effects of rupture.

Supposing no water to exist upon the earth, the square column under discussion might attain a notable elevation. The average land surface now stands about 4 kilometers or two and a half miles above the average sea bottom, and if the material from which the salt of the ocean has been derived represents eroded continents of present area, the average land surface might have stood some 2.5 kilometers higher than it now does. Whether so lofty a mass could sustain its own weight need not be discussed here, the present object being merely to bring out a particular feature of the whole problem.

The internal temperature of the continental mass likewise calls for consideration. At the present day the mean depth of the ocean is about 3,496 meters, the mean elevation of the land is about 440 meters and the mean thermometric gradient 1 degree in 38 meters, or possibly as high as 1 degree in 32 meters. The temperature at the bottom of the sea is not far from zero, while at the same level beneath the continents it is over 100 degrees. Thus the mean temperature of the actual continents down to the level of sea bottom is more than 50 deg. Cent. above the temperature of the sea-bottom itself, while for a long distance below this level the sub-continental masses must be hotter than the sub-oceanic layers. (Even if no energy were dissipated within the continental plateaus, the rate at which heat would be conducted from the subterrestrial to the sub-oceanic regions would be exceedingly low.)

Some of this temperature excess is probably a remnant of the original temperature of the globe, equivalent to that which has failed to escape because of the low diffusivity of the continental rocks. Another portion, probably considerable, represents kinetic energy dissipated in crushing and plication of the continental mass.

On the hypothesis under discussion all of this temperature excess and all of the energy of position represents heat which would have been radiated into space had all areas of the earth's surface been endowed with equal diffusivity.

\* A paper presented by George F. Becker of the United Geological Survey before the National Academy of Sciences, and published in its *Proceedings*.

<sup>1</sup> Simultaneous joints. *Proc. Wash. Acad.*, 7, 726 (1905).

<sup>2</sup> Becker, *J. Wash. Acad.*, 4, 429 (1914).

The outer shell of the earth down to a depth of perhaps 70 or 80 miles at which the primeval temperature still prevails without sensible diminution may thus be regarded as an imperfect heat engine, receiving heat energy at an absolute temperature approaching 2,000 degrees, and emitting it at less than 300 degrees. The difference is proportional to the energy which would be available were this engine perfect. Though far from perfect it has sufficed, it seems to me, to supply what has been expended in maintaining in part the relatively high temperature of the sub-continental masses, and also in epeirogenic and orogenic upheavals, in the shattering and crumpling of rocks, and in earthquakes and volcanoes. (It is to be expected that the dissipation of energy would be peculiarly intense near the surface, dividing the rising continental columns from the oceanic basins. It is in such positions that most of the volcanoes are found.)

So far the ocean has been practically ignored, but only a few years can have elapsed after the consistent status before the sea came into being. Even a very small difference in diffusivity, acting for a very short time, would have served to outline depressions into which the incipient ocean would gather while, after a time at any rate, the presence of the ocean with its convective circulation would tend further to increase the difference in temperature between the areas of relatively great and relatively small diffusivity, which would then become oceanic basins and continental plateaus.

The moment an ocean formed, or rather a moment before it began to form, erosion commenced and introduced a new factor into the world system. Were the globe completely covered by the sea, evaporation and precipitation would furnish no energy of geological significance. The energy absorbed in evaporation would be liberated on precipitation, and the molecules of water would return to their original level. But water falling on a continent and carrying sediment to the sea deposited or sets free the energy of position acquired at the expense of the heat stored in the earth.

At great depths we know that rocks are deformed and undergo solid flow; and it is well known that under an appropriate system of stresses any solid must flow.<sup>3</sup> At the surface, so far as rocks are concerned, such a system of stresses does not exist, and the rocks do not flow. But erosive action lends them a mobility almost equivalent to fluidity, so that the net result is in some respects analogous to that which would ensue if the solid surface of the globe were replaced by a mass of hyperviscous liquid, some column or columns of which had a higher temperature than the surrounding matter. These columns would rise above the general surface because of the diminished density and the mounds thus formed would overflow or run down because they lack rigidity. The outflowing portions would cool, and sinking into general mass, would establish a convective circulation.

Not just in the same way, but similarly, erosion effects the flow of the continental surface matter to or beyond the edge of the continental plateaus, overweighting the ocean floor and bringing about a corresponding subsidence.

In an asphalt lake like that of Trinidad convection due to lack of temperature equilibrium would be tended by an undertow. Material rising from any particular depth would diminish the horizontal pressure, which it had previously exerted on surrounding portions of the hyperviscous mass, and these would press inward to fill the partial void. In a solid earth there must be an analogous action, excepting that the partial pressure needful to produce lateral flow or undertow must exceed that which would strain the solid rock to its elastic limit.

The analogy of an asphalt lake must not be applied without caution. In such a lake it is easy to conceive of convective circulation indefinitely continued. Not so in the solid earth. If the whole rock mass from which the oceanic salt has been derived was really once piled on the continents, and if the ocean is  $100 \times 10^6$  years old, then the total uplift of about 6½ kilometers has only been effected at the rate of 1 millimeter in 15 years or 1 inch in 380 years. Thus the process might be compared with *incipient* convection in an asphalt lake.

None the less, so far as it has gone, the undertow has tended to contract the area of incipient continents, to increase the crumpling and to exaggerate the elevation

to which they would have attained had there been no convective tendency.

On the hypothesis that the origin of continents is due to the inferior diffusivity of certain areas of the earth's surface, the conditions of the ocean's bottom is very noteworthy. As is well known this floor is relatively featureless, consisting of vast plains, low ridges, and a few deeps, seven-eighths of its area lying at a depth of more than a kilometer below sea level. There are very few indications on the ocean floor of continental topography, and yet if a continent were to be submerged to a depth of a hundred fathoms or more, that is below the reach of wave action, it is difficult to see how any process of base-leveling could reduce its accentuation. Neither on the hypothesis under discussion is it easy to see how a continent could be submerged, though it is barely possible that a thin layer of rock of small diffusivity might be removed by erosion, leaving exposed masses of diffusivity so high as to undergo rapid contraction. Judging from the bathymetrical maps there are no important cases of this description, it would seem that, as the elder Dana so ably maintained, the oceanic areas have been persistent; and if so the subsidences which have occurred and recurred have been subordinate features of movements the net result of which in each case was uplift. This is in line with the results of Hayford, Helmert, and their associates. Since they have compelled us to concede that the earth is even now in a condition of approximate isostatic equilibrium, it seems impossible to believe that it has not been so in the past. Erosion has been in progress during every era from the Algonkian upward, and there must have been a persistent and prevailing tendency to upheaval. Of a complete drowning of the continents, such as would occur during a prolonged era in which subsidence prevailed, there is now no trace.

Two reasons have been suggested above for the high level at which the continents stand relatively to the ocean floor, viz., superior temperature and the existence of voids. The difference in level is 3.936 kilometers or 0.032 of 122 kilometers. If this difference were entirely due to excess of temperature, and if the linear expansion of average rock is 0.0008 per degree, the whole elevation of the continental columns would indicate a mean temperature of difference of 40 deg. Cent. If this elevation were due entirely to the existence of voids these would amount to about half the maximum interstitial space found for me by Mr. Melcher in experiments on the crushing of sulphur in sealed brass tubes. It is evident that the two causes in combination might bring about elevations not only corresponding to the mean height of the continents, but also to those of lofty mountain ranges.

Until erosion began the terrestrial mechanism must be regarded as a heat engine of the irreversible type. It could potentialize energy and do mechanical work, but the cycle was incomplete. When erosion supervened and conferred upon the superficies of the continents a certain mobility and kinetic energy, the cycle was completed and the stage answering the adiabatic expansion was supplied.

It is true that the efficiency of this engine must be very small, but the store of energy upon which it draws—the available boiler capacity—is enormous. The mechanism thus appears competent to bring about all of the dynamical effects with which geology has to deal.

### Measurements of the Planet Saturn

FROM a photograph of the planet Saturn taken by Barnard at Mount Wilson in 1911, with the 60-inch reflector, using an equivalent focus of 100 feet, P. H. Hepburn has made a series of measurements. Several striking discrepancies are shown by these photographic dimensions from the values derived by several observers visually, and a plotted chart of the ring system brings this out very clearly. In the discussion as to the cause of the difference, it is considered whether it may be due to systematic errors in the micrometric movements of convex compared with concave outlines, or differences in the photographic or visual images; or physical changes in the planetary system. An interesting statement is that the author finds evidence of the transparency of the ring A, and also that its surface is not uniformly bright. An old report by Trouvelot in 1855 is quoted showing that the transparency of the ring A was suspected at that time. Full details are given of the measures of the system in *Roy. Astronom. Soc. M.N.*, 74, p. 721.

# Automobile Lubrication—I\*

## How to Test, and How to Use Various Classes of Oils and Greases

By C. W. Stratford

During the infancy of the automobile industry engineers and operators of motor vehicles had their hands full to keep their machines going at all. Consequently, they had little time or inclination to study the subject of proper lubrication. But as the use of internal combustion engines for the propulsion of automobiles, motor-

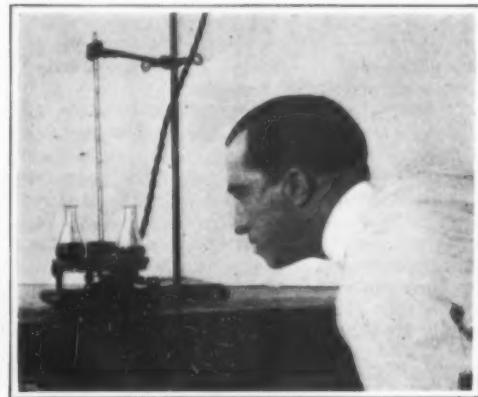


Fig. 3.—Heat test.

cycles, agricultural tractors, etc., became more universal, and as other operating troubles were finally eliminated one by one, the question of correct lubrication gradually and naturally came to the front with a pertinent plea for attention.

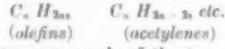
The subject of heat motor lubrication, complex as it is, can perhaps best be presented by first considering the chemical and physical properties of the lubricants themselves and the refining processes.

### CHEMICAL STRUCTURE OF HYDRO-CARBON MOTOR OILS.

The term "non-carbon" frequently used in the oil trade, obviously for the purpose of misleading the buying public, is not only a misnomer, but a statement contrary to chemical fact. Lubricating oils are hydrocarbons and, as their name indicates, consist of a physical mixture of different chemical compounds of the element carbon and the element hydrogen. No other elements are present except as impurities. Just as cream, butter, cheese and other products are derived from milk, so are hundreds of different hydro-carbon compounds, lying between the extreme limits of gasoline and cylinder stocks or coke, separated from crude oil. Each one of these many compounds has its own peculiar physical properties, such as definite boiling points, etc. American motor oils are manufactured from paraffin, asphaltic, and mixed paraffin and asphaltic base crude oils. The limitations of this paper preclude a lengthy discussion of the exact chemical structure of compounds found in crude oils of different bases, further than to say that paraffin base oil belongs to the methane series, characteristic formula



while the asphaltic base oils are composed of the series of hydro-carbons containing more carbon to the molecule (unsaturated), characteristic formulae:



In addition to compounds of the two principal series, many other different compounds are found in paraffin and asphaltic base oils in variable quantities, depending upon the source of the crude. Russian oil is made up

\* A paper presented at the Semi-annual meeting of the Society of Automobile Engineers, June 14th-17th, 1915.

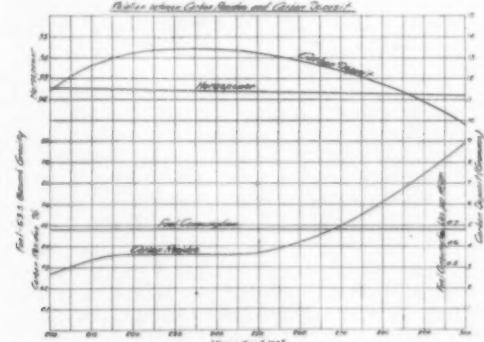


Fig. 6.—Relation between carbon residue and carbon deposit.

largely of hydro-carbons of the naphthalene series, characteristic formula



Motor oils refined from crude oils of different bases present a very marked difference with regard to their physical properties and chemical stability.

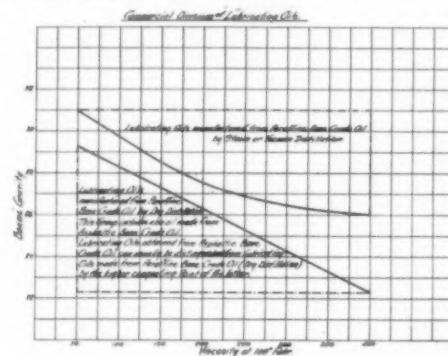


Fig. 1.—Commercial divisions of lubricating oils.

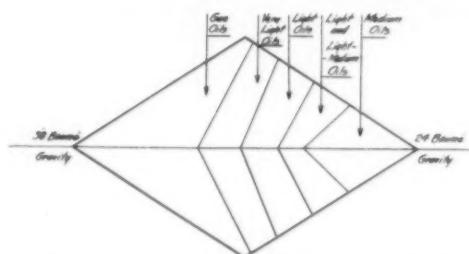


Fig. 2.—Separation of the lubricating distillate.

### SEPARATION INTO GROUPS BY DISTILLATION.

Simply stated, the preparation of motor oils consists of a separation of a certain body of compounds which have as a mean the properties required of motor lubricants. All hydro-carbon oils are prepared for the market by one of the two following methods (a) steam or vacuum distillation, (b) dry or destructive distillation. The commercial division chart (Fig. 1) shows a classification of paraffin and asphaltic base oils refined by these two processes. It will, no doubt, also be of interest to many to learn how motor oils are separated, according to their gravities and viscosities, from the "lubricating distillate." The areas within the quadrilateral (Fig. 2) indicate graphically the volumetric and gravimetric separation of this distillate into its market forms. It will be seen that the motor oil area represents a remarkably small percentage of the total area, all of which accounts for the higher price of high-grade finished motor oils compared to other products.

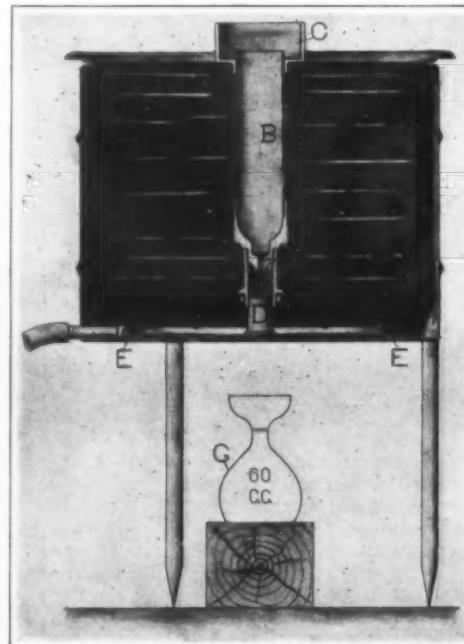


Fig. 7.—Sayboldt universal instrument.

### REFINING PROCESSES.

**Sulphuric Acid Process.**—By this process after the separation of the lubricating distillate into groups, the lubricating oil fractions are treated with sulphuric acid to throw down unstable compounds, free carbon, etc., washed thoroughly with water, neutralized with an alkali

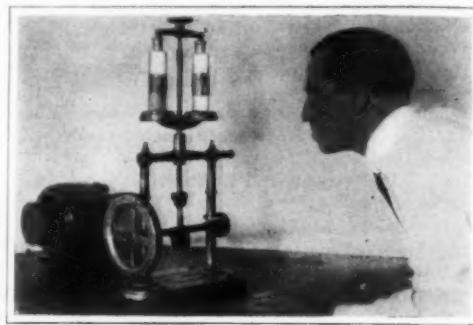
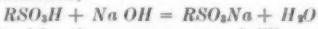
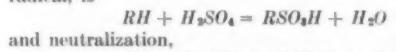


Fig. 4.—Emulsion test.

and the whole again washed and separated. The oil remaining is then blown with air to remove traces of water that may be present. Another method consists of filtering lubricating oil fractions, which have been partially decolorized by sulphuric acid to complete the decolorization necessary to bring them up to marketable standards. Such oils may be technically called "filtered" oils. The interesting reaction here, due to the sulphuric acid, letting  $R$  represent the hydro-carbon radical, is



Oils refined by these processes are brilliant to the eye and they all contain hydro-carbon sodium "sulpho" salts, varying in quantity with the quality of the oil considered. The effect of the presence of this compound will be studied later.

**Filtration Process.**—After the separation of motor oils from the "lubricating distillate," they are filtered through Fuller's earth which removes impurities and hydrocarbons of high carbon content. Filtered oils of first-class quality contain no "sulpho" compounds.

### CHEMICAL REQUISITES OF MOTOR OILS.

To obtain maximum lubricating efficiency and maximum durability, it is imperative (1) that motor oils contain a minimum quantity of unsaturated hydrocarbons, to prevent rapid polymerization and "cracking," and (2) that the oils contain no "sulpho" compounds or other impurities as a guarantee against the rapid accelerating effect which such acid compounds exert when exposed to heat, upon polymerization and sedimentation. The proper methods of making the heat and emulsion tests to determine the presence of sulphonate compounds are as follows:

**Heat Test.**—Fill a clean bottle or a small Erlenmeyer flask about half full with the oil to be tested. Heat it up slowly over an open flame or on an electric plate (Fig. 3) until yellow vapors appear above the surface of the oil. (The temperature at which these vapors appear will depend upon the flash point of the oil tested.) Hold at this temperature for 15 minutes. A comparison of the heated with an unheated sample of the same oil tells the story of quality. Good oil darkens in color, but remains perfectly clear and without sediment, even after standing 24 hours, thus proving the total absence of acid compounds. Impure oil, on the other hand, turns jet black. If allowed to stand 24 hours, a black

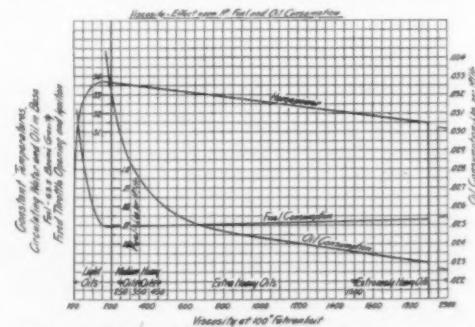


Fig. 8.—Effect of viscosity on horse-power, fuel and oil consumption.

carbon-like sediment settles out, proving the presence of sulphuric or sulphonate acid compounds. This test is so unfailing and so important, that I would recommend it to oil purchasers as a feature to be incorporated in their specifications.

*Emulsion Test.*—(To be made with 100 per cent hydrocarbon oils only). Fill a bottle (preferably 4 ounces) one third full with the oil to be tested. Pour in an equal amount of water, leaving a space of one third free above

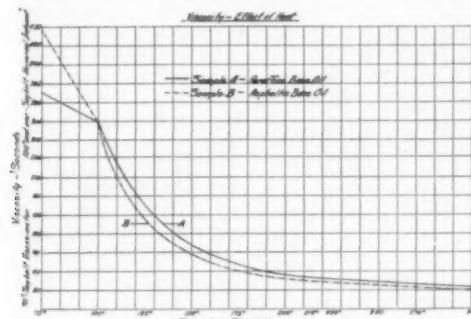


Fig. 9.—Effect of heat on viscosity.

the oil and water. Cork and shake the bottle vigorously 30 minutes in a shaking machine or by hand (Fig. 4). Then set it aside for 24 hours. Good oil shows a fine white line of demarcation between the oil and clear water below, indicating the absence of acid compounds. Impure oil mixes permanently with the water, appearing as a curdled mass, floating upon milky water below. This indicates the presence of sulphuric or sulphonate acid compounds. The curdled portion is a sort of sulphuric acid soap, and the amount of the curd shows the quantity of "sulpho" compounds present. The object of this test is exactly the same as that of the heat test, with the disadvantage that it requires more time. To engineers and others making a study of oils it is worthy of notice, because of the fact that there is a certain quantity of water present in the crankcase of motors, due to the condensation of the products of combustion.

#### SIGNIFICANCE OF PHYSICAL PROPERTIES.

Four properties only need be recorded as essential in judging the qualities of oils for use in internal combustion engines, Flash Test, Carbon Residue, Cold Test and Viscosity. In addition the Gravity, Fire Test and Color are also considered at the refinery and to some extent in the trade (Fig. 5).

*Flash.*—By definition the flash point of an oil is the lowest temperature at which the vapors arising therefrom ignite without setting fire to the oil itself when a small test flame is quickly brought near its surface in a test cup and quickly removed. Inasmuch as the temperature of explosion exceeds by several times that of the highest obtainable flash it is clearly apparent that even 100 degrees difference in the flash of two oils can be of no avail in resisting destruction within the explosion chamber. Below the pistons, however, the operating temperature of piston heads and other parts requires the use of high-flash oils for reasons of economy and durability. Motor oils having a flash point much below 400 deg. Fahr. show a very appreciable vaporization loss by way of the breather orifices. This loss increases rapidly with a further drop in flash and increase in crankcase temperature.



Cold test.

*Carbon Residue.*—There is a certain amount of carbon in all motor oil which can be "fixed" by distilling a given quantity, in a standard flask and at a uniform rate, to the end (Gray method: 25 cubic centimeters, rate one drop per second, destructive distillation). A coating of carbon will remain upon the walls of the flask which is weighed and the percentage of carbon determined. This "fixed" carbon is termed carbon residue and is not to be confused with carbon deposit. In commercial oils the carbon residue increases nearly in proportion to the increase in viscosity, being lowest in the very light oils. The carbon residue, high or low that an oil contains does not necessarily indicate the relative amount of Carbon Deposit (Fig. 6), which will occur, in use, on the explosion chamber walls of a motor. Carbonization is also greatly influenced by the quality of the oil, by its viscosity and flash and by piston-ring leakage. If a motor must be operated with leaky piston rings, then an oil of the lowest possible carbon residue will leave behind the least volume of carbon deposit.

*Cold Test.*—The chill or cold test of an oil is the lowest temperature at which it will pour. This characteristic need only be taken into consideration in regard to its effect upon the free circulation of oil through exterior feed pipes and sight gages, where pressure is not applied. The cold test is in no way indicative of lubricating or heat-resisting qualities.

*Viscosity.*—The viscosity (cohesion) of an oil is usually given in terms of time. The number of seconds required for a definite volume of oil under an arbitrary head, to flow through a standardized aperture at constant temperatures (Fig. 7). Readings are commonly taken at 100 deg. and 212 deg. Fahr. In all phases of lubrication the matter of correct viscosity is one of prime importance and its effect is far-reaching. The curves shown in Fig. 8 will point out the effect that viscosity has upon horse-power, and fuel and oil consumption.

*Effects of Viscosity.*—Even the veriest novice can readily note the difference between the power and rapidity of acceleration of his motor when using a light or medium oil (180 to 350 seconds) as compared to an extremely heavy oil (2,300 seconds). When oils lighter than 180 seconds are used the horse-power falls off very rapidly until the pistons and bearings finally seize, with oil of approximately 100 seconds.

It will be seen that the fuel consumption reaches its minimum when a light oil of about 180 seconds is used. Oil of this viscosity gives the maximum horse-power obtainable with a given engine. As the viscosity increases from 180 seconds the fuel consumption increases uniformly with it. With oils below 180 seconds

seconds the fuel consumption mounts to its maximum.

Considering the curve of oil consumption a most extraordinary variation in the quantity of light and heavy oils burned will be remarked. Between 800 and 2,300 seconds the variation is comparatively slight, a

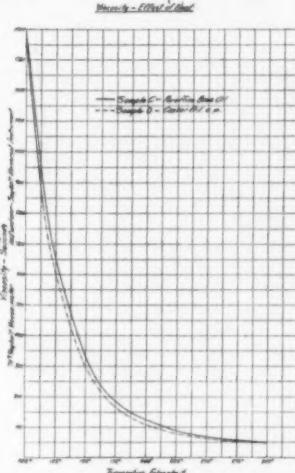


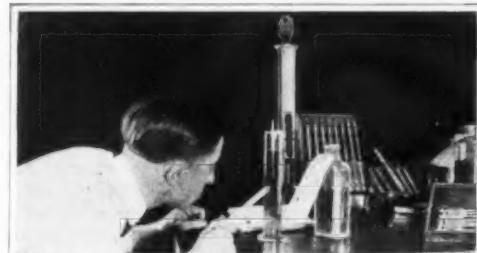
Fig. 10.—Effect of heat on viscosity.

fact which indicates that there is no advantage to be gained by the use of oils heavier in body than 800 seconds. Passing from 800 to the light oils it becomes evident at once that there must be some point (viscosity) where the highest economy of both fuel and oil is attained together with high horse-power. Both laboratory and service tests on the road have demonstrated that this point lies between 300 and 800 seconds and that it depends directly upon the condition of the motors in which the oils are used and upon their average operating temperatures. Were it not for the difficulty of a more rapid carbonization (when heavy oils are used) no oil having a viscosity of less than 300 would be recommended, in the light of these facts. But a practical compromise must be reached; consequently light and medium oils (180 to 300 seconds) are regularly specified as being the most fool-proof in character and hence best capable of meeting the most widely differing conditions of service.

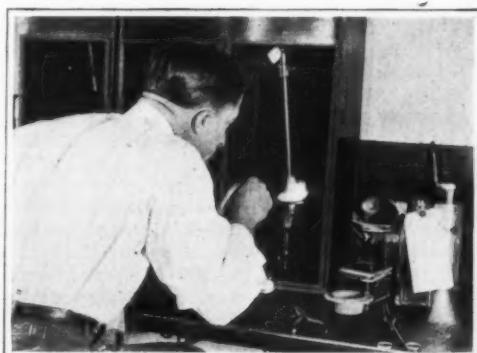
#### EFFECT OF HEAT UPON VISCOSITY.

All motor oils when heated become thinner and thinner or in other words lose in viscosity. The rate of this loss, with rise in temperature, is not uniform, nor is it comparative between oils of very light and very heavy body. In addition, oils of different chemical make-up, but of the same body at 100 deg. Fahr., show a decided divergence in viscosity at higher temperatures. Curve A (Fig. 9) represents a paraffin base oil and B an asphaltic base oil. Though the viscosity of both is equal at 100 deg. Fahr., the viscosity of the asphaltic base oil falls off at a more rapid rate and remains below that of the paraffin base oil throughout the entire range up to 300 deg. Fahr. Curves C and D (Fig. 10), representing a heavy paraffin base and chemically pure castor oil respectively, denote the comparative rate of loss in viscosity up to 300 deg. Fahr. These curves seem to indicate that castor oil possesses no advantages over paraffin base mineral oil for use in high-speed racing motors.

(To be continued)



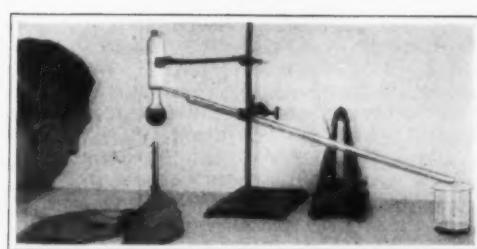
Gravity.



Fire.



Flash.



Viscosity.



Carbon residue.

Fig. 5.—Testing a lubricant.

# The Science of the Cipher

## And an Explanation of Bacon's Undecipherable System

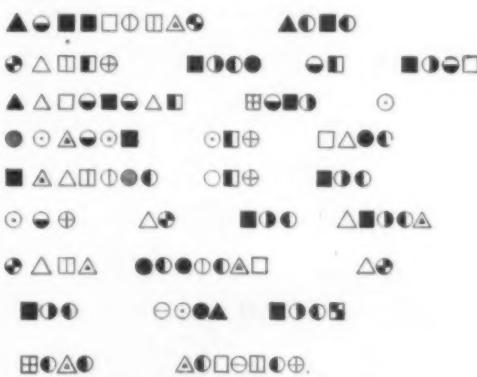
By William W. Brewton

THE creation and solution of cryptographs, or illusive writings, is an art which by no means has been confined to any particular period of letters. It is an art which was highly perfected by the Egyptian Ptolemies, and which has engaged the attention of royal secretaries from the very earliest times. It perhaps figures more prominently in fiction than elsewhere in modern times. Few writers to-day, who possess anything like an analytical turn of mind, fail to make use of the cipher, realizing that it has always been of wide interest to readers.

Edgar Allan Poe, a master in this sphere of thought, has asserted that "it may well be doubted whether human ingenuity can construct an enigma of the kind which human ingenuity may not, by proper application, resolve." However, Francis Bacon, Baron Verulam, who has been called the founder of modern science, once wrote that the art of deciphering was a work of labor and ingenuity—"yet by diligent precaution it may be rendered useless . . . for if the ciphers in use were good and trusty, several of them would absolutely elude the labor of the decipherer, and yet remain commodious enough, so as to be readily written and read."

It may be said that there are two general methods upon which a person who wishes to solve a cipher may enter: the gathering together and comparing those circumstances which seem to indicate the meaning and intentions of the writer, and the solution from the formation and arrangement of the very characters of the cipher themselves. Both of these processes, of course, are generally used before a complete solution is attained, but the decipherer will usually begin with only one—the method which his observation of the cipher indicates will secure the earliest solution. A solution from the very characters of the writing themselves is the method pursued when these characters are presented in some regular, related and suggestive form. When thus arranged, the decipherer will be able usually to ascertain the alphabetical key to the writing, and by applying this key throughout he may resolve the entire cipher.

As an illustration of the type of cryptograph which may be resolved from its form and appearance, the author will exhibit one which he once received from a former school-boy friend, written when this friend was still a lad of sixteen years, and with whom quite an extensive cipher correspondence was carried on:



### Specimen of simple cryptograph.

At the first glance at the above, the decipherer will observe that his task will be quickly ended, for the message is set out in a cipher whose form lends every aid. The words are separated conveniently, and there is a constant recurrence of similar characters, which clearly enough are the letters of words. At any rate the decipherer would proceed upon this simple plan until he saw that he had underestimated the complexity of the cipher. In reading this message, it would be noted at once that the first word is not the place at which to begin in search of a key. For the first step in arranging a key would be conjecture, or more or less certain guess-work, and the first word is too long, has too many letters, to be easily guessed at. The decipherer would naturally look for a word whose entire list of letters he might conjecture, and thus secure as quickly as possible the maximum number of letters in the cipher alphabet. He notes that there is one word of only one letter at the end of the third line. This will be either the word *A* or *O* or *I*. He guesses *A* because he has observed that in the very next line is a word of three letters, which suggests itself as *and*, and which

begins with the same character. Especially would he venture this conjecture when he notices immediately under this word another just like it. Inasmuch as the word *and* is one which occurs frequently, whether in short or lengthy messages, the decipherer feels reasonably certain that his guess is correct. With the three letters thus obtained, he now seeks for some other word containing them, or part of them, in order to substitute as far as possible, and conjecture the remainder of such a word. But before doing this he may reasonably guess that the word appearing at the end of the fifth line is *the* inasmuch as the same word occurs also in the very next line, when it is well known to him that *the* is a very frequent word in all writings, and that it is a word which very naturally follows the word *and*, which he has already obtained to a reasonable certainty. Now there would be no necessity of beginning a substitution of the letters reasonably obtained in other words, as long as there are a number of brief words to speculate upon. In the sixth line there is a word of two letters (the second word), which also occurs as the last word of the seventh line. The words *at*, *to* or *of* suggest themselves as probable, but we at once discard *at* and *to*, or even the word *on*, inasmuch as it is known that the letters *a*, or *t*, or *n* do not occur in the word which is being deciphered, inasmuch as it has already been ascertained that there are other and different characters representing them in other words. So it is concluded that the word must be *of*, against which conclusion there is no reasonable objection anyway. If we substitute the letters we have derived in the word at the end of the sixth line which seems to contain several of the conjectured characters, we soon obtain the word *other*, the letters *h* and *r* being the only ones we must again conjecture. This word is accepted as correct until it is proved not so. The third word in the second line is readily guessed as *in*, inasmuch as the second letter has been ascertained to be *n* and the first letter cannot be *o*, to make the word *on*, a character for *o* having been already ascertained.

By continuing to look for words containing ascertained characters, the decipherer notes the first word in the seventh line whose every letter he has decided except the third. By substituting the deciphered letters the word *four* is the only reasonable one which suggests itself, and one more letter, *u*, is obtained. By substituting in the first word of the fifth line the answer to it is the word *trouble*, it being necessary to conjecture only the fifth and sixth letters. Immediately under this word on the sixth line, the decipherer concludes the word *aid*, having obtained all the characters of this word in solution. The entire cipher is in two sentences and we may read a part of the second by substituting only a few other instances. We read, beginning at the first of the second sentence: "With a lariat and some trouble and the aid of the other four members of the." By proceeding with the method we have pursued, the entire solution becomes:

"Pittsburgh Pete found them in this position. With a lariat and some trouble and the aid of the other four members of the camp they were rescued."

The above cipher, of course, is one very easily solved but in solving it we illustrate the method which is used in the case of those ciphers which offer a key through their form or construction. By complicating the appearance of his message the cipher writer will render a thousandfold more difficult its solution. Where the words are undivided, conjecture of letters and short words is prevented. Yet Poe is very near the truth when he asserts that few consistent messages can be arranged which cannot be solved. If the message is of any reasonable length, the recurring character representing some alphabetical letter will finally suggest some meaning. With his solution, of course, the decipherer must correlate the principles of language, many of which are the same in all tongues.

For dispatch and convenience, ciphers are often written in war times by one general to another on the same side by simply writing out a number of sentences giving a particular direction, which in reality will have the opposite meaning from the one indicated by the message. If such a message should fall into the hands of the enemy, its solution would be attempted by proceeding to reason out the true message which was sent. The general circumstances existing at the time might indicate to the decipherer that instead of "attack" the message conveyed the order to "retreat", though the actual words of the message indicated the

former. It is the purpose of cipher writers in armies to convey in their messages as simple statements as possible, in order to free them from suspicion. In military affairs, and also in the secret affairs of State, complexity in ciphers excites suspicion, and attracts too much attention. The ability to convey convenient and accurate and easily interpretable secret messages, in regular language and in ordinary sentences, is the art which is to-day sought by those who must necessarily use the cipher.

A highly useful, and at the same time practically undecipherable, scheme for cipher writing was invented by Bacon when a youth of about seventeen in Paris. It is a method of expressing, as he termed it, "anything by everything," and the only condition or limitation placed upon its use is that the matter included be five times less than that which includes it. This condition arises by reason of the fact that each letter of the cipher alphabet is represented by five letters of the writer's ordinary alphabet. Five letters are chosen because this arrangement will admit of 32 changes, and therefore will embrace a change for each of the 26 letters of the English alphabet. Bacon's arrangement is as follows, the changes of five places being represented with the use of only two letters:

A is represented by	aaaaa	N is represented by	abbaa
B "	" aaaaab	O "	" abbab
C "	" aaabba	P "	" abbbba
D "	" aaabb	Q "	" abbbbb
E "	" abaaa	R "	" baaaa
F "	" aabab	S "	" baanab
G "	" aabbba	T "	" baabaa
H "	" aabbbb	U "	" bbbbbb
I "	" abaaa	V "	" baabab
J "	" bbbba	W "	" babaaa
K "	" abaab	X "	" babbab
L "	" ababa	Y "	" babbaa
M "	" abbaa	Z "	" babbaab

Under this scheme, for example, if we should wish to write the word Fly, it would be thus formed:

F	L	Y
aabab	ababa	babba

Suppose also that there be adopted two forms of letters, as for example the Roman and the Italic, and that each Roman letter represent A and each Italic letter represent B. Then a cipher of the above plan could be woven into a message of one's natural and usual vocabulary. One could send a message to "fly," for instance, by sending the words, "Stay till I come to you." The message with its interpretation would be thus:

The message with its interpretation would be that

<b>aabab</b>	<b>ababa</b>	<b>babba</b>
<i>Stayt</i>	<i>illico</i>	<i>metoyou</i>

though, of course, the message sent would be simply

though, of course, the message sent would be simply :  
*Stay till I come to you.*  
There would be here no significance to the final *or* in the sentence, but the person to whom the message would be sent would have no difficulty in extracting the real, internal message. In case the cipher were written by hand, with pencil or pen, the italicized letters could be indicated by underscoring at the proper place. In order to render the message still more difficult to solve, it might be lengthened into one of twenty-five or fifty words, underscoring or leaving plain in the non-significant places in such a manner as make them of no effect, and therefore to keep them from conflicting with the words which convey the secret message. For instance, if we follow the plan of letting italicized letters represent B, and the plain letters represent A, the internal message : "We retreat at midnight," is conveyed in the following :

General Greig advances upon the enemy's left at daybreak. Throw your right in position to cover his prospective retreat, and engage the enemy's right if he holds his ground.

For convenience it may be agreed that all secret messages shall begin with a certain letter of the obvious and visible writing. For example, in the above we begin the secret message with the thirteenth letter, *a* in advance. From that letter down through the word, *engage*, is a significant arrangement conveying the message, "We retreat at midnight." If the message begins with some definitely determined letter by number, the person to whom the message is sent can thus disregard from the beginning all that part of the writing up to that point. It might be agreed that the secret message begin with the thirtieth word, for example; and thus allow considerable difficulty for the illegitimate decipherer before he even approaches any significant part

of the writing. To render the matter still more complex, the persons carrying on the secret correspondence might adopt the pre-arranged plan that every fifth word shall be significant, or that there shall be a significant word after the first twenty words of the visible writing and then there shall be thirty non-significant words to be followed by fifteen significant ones to be followed by forty non-significant. Of course all non-significant words shall be written with Roman and Italic modifications, just as the significant ones, in order that there shall be room for no suspicion upon any particular part of the writing. Before the word *advance*, and after the word *engage*, in the above cipher, the words are non-significant, though presenting an appearance similar to the other parts of the writing. By translating the Italics into B's and the Romans into A's in *General Greig*, for example, and then grouping five letters in one place to make a letter of the true message, it is found that the arrangement furnishes nothing of any meaning, and such parts of the writing, of course, the person receiving it may disregard. The greater the length of the writing, compared to the length of the inner message, the more difficult will be a solution by a person who does not know the plan of forming it; which is directly contrary to what is true concerning such a cipher as is found in Poe's *Gold Bug*, or any cipher which may be resolved by observing its form and construction. A cipher of individual unknown characters, if consistent throughout, will be the easier to resolve, the greater its length; inasmuch as

in resolving it one would wish to observe the characters related in as many different ways as possible. While a cipher which must be resolved by ascertaining the circumstances associated with it, and deducing from them its meaning, will be the easiest of solution when it is briefest, when there are fewer conflicting ideas and fewer words. In the cipher above, the form would be suggestive to the decipherer as well as any conclusions he might attain from its visible wording and from the meaning of the visible writing itself, for the modified shape of the letters would indicate some significance. However, where the letters of both the ordinary and the secret messages are alike, and the one is simply folded, or secretly placed, within the other, form indications do not mean very much to the decipherer, and a cipher arranged on this plan will prove itself the most difficult of solution. If time for arranging a cipher message were of no consequence, it would be a fairly easy matter for one to arrange a secret message within a visible writing and place thereon no form indications at all. For instance, instead of determining B's by an Italic letter and A's by a plain letter, it could be adopted, as a pre-arranged plan between the corresponding parties, that every letter in the visible writing which is followed by a consonant shall be an A, and every letter followed by a vowel shall be a B; or that every letter of the writing followed by one of the first thirteen letters of the alphabet shall be an A, and where followed by one of the last thirteen letters of the alphabet it shall be

a B. But to so frame an outer writing as to accommodate this highly restricted arrangement would be impracticable both because it would require too much time to do so, and because at times it would be necessary to use words whose meaning would be not at all connected with that of the rest of the writing, in order to come within the pre-arranged sequence of letters. A plan of this kind could be made and used where the correspondents have no demand of dispatch, either in writing or reading, upon them; but for practical purposes, as war or hasty diplomatic correspondence, the writer and reader must avoid such delays as this plan imposes. The writer desires to be able to write out his message instantly upon forming it in his mind without having to run through all the words he can call to mind in order to use those which will conform to any plan. By using the biliteral alphabet of Bacon's the cipher writer may make any exterior writing convey any secret message, and obviously this plan is the one which has the greatest facility and which is, therefore, the most practical. The question of how the A's are to be determined from the B's is a matter which should be left to the correspondents themselves, any plan of marking the visible letters being practical so long as it may be observed by the reader, whether clever enough to elude the notice of the illegitimate decipherer or not.

For practical cipher writers, the objective is adaptability to circumstances and freedom from unique or suspicious appearance.

### Coal Mined by Machines

THE substitution of mechanical methods for hand labor in the bituminous coal mines of the United States during the last quarter of a century has been one of the most interesting features connected with that branch of the coal-mining industry. It would have been a physical impossibility to have attained the present enormous production of bituminous coal (nearly half a billion tons in 1913) if it had been necessary to depend upon hand labor alone. The results accomplished by the use of mining machines are threefold: (1) The exacting character of the miners' employment is much ameliorated; (2) the percentage of lump coal is increased, which means a better average price for the total product; and (3) the cost of production is reduced. The first is of a humanitarian character, but the two last, which are purely economic, have been the chief incentives in the changing of mining methods which has made the mining of bituminous coal in the United States during the last twenty-five years an epoch in the history of the industry. In many cases the installation of mining machinery has been forced upon the operators by the constantly advancing cost of labor and the necessity for keeping mining expenses within the lowest possible limits because of the keen competition and the low selling prices which have existed for many years in the principal coal-producing States. In 1890, the first year that the statistics of labor employed in the coal mines of the United States were collected and when the use of mining machines were just beginning, the average production of bituminous coal per man employed was 579 tons and the total production was 111,302,322 short tons. In 1913 the mine employees averaged only six more days in the year, the average production per man was 837 tons, and the total production was 478,523,203 short tons, about 4.3 times that of 1890. But in 1913, 242,476,559 tons, or a little more than 50 per cent of the total, were machine-mined, whereas in 1890 probably less than 5,000,000 tons (not 5 per cent of the total) were machine-mined. At the same rate of production per man as in 1890, the total output of bituminous coal in the United States for 1913 would have been about 331,000,000 tons or about two thirds of the product actually won. If the bituminous mines had worked full 300 days in 1913 the production would have amounted to over 618,000,000 tons.

The total production of bituminous coal in the United States increased from 450,104,982 short tons in 1912 to 478,523,203 tons in 1913. The quantity of coal undercut or otherwise mined by the use of machines increased from 210,538,822 tons to 242,476,559 tons. The increase in the total production was 28,418,221 tons, or 6.2 per cent, and the increase in the output by the use of machines was 31,937,737 tons, or more than 15 per cent. The increase in the production of machine-mined coal exceeded the increase in the total production by 3,519,516 tons. The percentage of machine-mined coal to the total output has increased each year since the first successful mining machines were installed. In 1903, ten years prior to the period covered by the present report, the quantity of bituminous coal mined by machinery in the United States represented 27.6 per cent of the total; in 1910 it was 41.7 per cent; in 1911, 43.9 per cent; in 1912, 46.8 per cent; and in 1913, 50.7 per cent.

During the last few years there has been a general complaint of shortage of labor in the bituminous fields,

a condition favorable to further advances in mining wages and to the more extended use of mining machinery to offset them. It is to be expected, therefore, that the production of coal by mechanical methods will continue to show proportionate increase until a relatively small quantity will be mined by hand. In addition to the economic and humanitarian results accomplished by the use of machines, another important end is attained. The larger the proportion of coal mined by machines the smaller will be the proportion of coal shot off the solid without having been previously mined or sheared. Any step which mitigates that evil in the mining of bituminous coal is a step in advance, and as shown in the section on mining methods in this report, there was a reduction in the percentage of coal mined by powder. Recent developments in the construction of mining machinery have provided machines which are adapted to beds of any inclination, so that there are now practically no insurmountable physical obstacles to the substitution of machines for hand labor.

The methods of attacking the coal by machinery are of two distinct types. One is that of sawing; the other, of chopping. Three types of machines represent the former method—the chain-breast, the long-wall, and the short-wall. In these machines the coal is attacked by bits attached to an endless chain or to the periphery of a disk; and, as can be readily seen, the action is very similar to that of sawing wood. In the second type of machine the coal is attacked by bits attached to arms actuated reciprocally, as in the action of drilling, except that the work of the drill is not confined to one hole, but is freely changed at the will of the operator. These machines are designated as the pick or puncher, in which the drill is mounted on two wheels and operated on a platform in front of the face of the coal, and as the radialaxle or post-puncher, in which the piston is attached to a post and drill is radiated in one plane. This latter machine has been developed for use in the steep-pitching beds. A new machine, brought out in 1912, combines the sawing and the chopping actions of the other two types. In this machine bits are inserted in the manner of a screw around an arm projecting from the machine. This arm is given both a reciprocating and a revolving motion, so that the coal is attacked by both a chopping and a sawing action. This machine was not actually placed on the market until 1913.

The total number of machines reported in use in the bituminous coal mines of the United States in 1913 was 16,381, an increase of 1,063 over 1912, when the number of machines reported was 15,298. The average number of tons mined by each machine in 1913 was 14,802, against 13,763 in 1912, the average for 1913 being the largest tonnage per machine reported. The best record prior to 1913 was in 1890, when the average production per machine was 14,068 tons. The most popular types of machines now in use are the pick or puncher and the chain-breast, the latter being in somewhat more general use in 1913; in 1912 the larger number of machines used were punchers. Out of the total of 16,381 machines in use in 1913, 6,936, or 42.3 per cent, were chain-breast; 6,327 were punchers; 2,210 were short-wall; 791 were long-wall; and 117 were of the radialaxle or post-puncher type. The rapid gain of the short-wall machine in popularity is referred to in the report for 1912, and it continued in 1913, the number of this type of machine having increased from 1,371 to 2,210, a gain

of 830, or 60 per cent. Pennsylvania, the largest producer of bituminous coal, is also first in the total tonnage mined by machines and in the total number of machines in use. West Virginia, the second State in coal-producing importance, ranks also second in the number of machines in use and in the tonnage won by them; but the credit for the largest percentage of machine-mined coal to the total output belongs indisputably to Ohio, whose output of coal mined by machines in 1913 was 90.2 per cent of the total production. In 1912, 87 per cent of Ohio's production was machine-mined. Kentucky ranks second in the percentage of the total product mined by machines with 73.2 per cent in 1913, against 66.4 per cent in 1912. Michigan's percentage of machine-mined coal increased from 52.7 per cent in 1912 to 70 per cent in 1913. West Virginia, Pennsylvania, and Indiana were each credited with more than half of their total production mined by machines in both years, and Illinois had 53 per cent in 1913, compared with 45 in 1912. In 1913 Pennsylvania's production of machine-mined coal was 92,487,438 short tons out of a total of 173,781,217 tons. West Virginia, with a total production of 71,308,982 tons, reported 39,410,264 tons mined by machines; Ohio, with a total production of 36,200,527 tons, reported 32,642,848 tons as mined by machines. Illinois's production of machine-mined coal was 32,630,555 out of a total of 61,618,744 tons; Indiana reported 9,737,425 tons as machine-mined out of a total production of 17,165,071.—*Mineral Resources of the United States for 1913, Department of Interior, by E. W. Parker.*

### A Motorcycle Street Sweeper

ONE of the latest American novelties is a motor cycle street sweeper, says the *Motor Cycle*. It is mounted on a sidecar chassis of peculiar design, and in front of the sweeping mechanism is a steel brush which acts as an agitator for the purpose of loosening the dirt, so that the broom will easily remove it. The broom is lowered by means of a handle situated on the left of the driver's seat and when the broom is in contact with the pavement it engages the actuating mechanism connected to the sidecar wheel, which causes the broom to rotate. Raising the broom throws the mechanism out of action. It is designed to be used on asphalt or wood-paved streets. At present one of these machines is in operation in Washington, and owing to its satisfactory operation its use is likely to be extended.

### Ancient Wax Seals

INTERESTING results obtained by the Government chemist by making analyses of old wax impressions on documents in the Public Record Office are described by Mr. Ainsworth Mitchell in *Knowledge*. The seals examined dated from the thirteenth to the eighteenth century, and differed but little from modern sealing wax. Most of them consisted of a mixture of beeswax and resin, others of pure beeswax. Two seals, of the dates 1399 and 1423 respectively, were composed of wax, the characteristics of which agreed more nearly with those of East Indian than of European beeswax. The wax composing an impression from the Great Seal of 1350 agreed, in chemical and physical characters, with pure beeswax of to-day. The pigment in the red seals was vermillion, while the green seals contained verdigris.

# A Stop Motion for Moving Picture Machines

## An Ingenious and Radical Improvement

By W. B. Morton

EVER since intermittent movement has been in use particular efforts have been made to make the movement of such characteristic that the least amount of strain would bear on the part to be moved.

In a continuous movement no force is required for the maintenance of the movement except to overcome incidental friction and windage.

In an intermittent movement, however, considerable forces are required to accelerate the masses from standstill to maximum velocity, and then again to retard the same masses from that maximum velocity to a standstill. If the accelerating force is constant during the whole time of acceleration a uniformly accelerated movement ensues.

The simplest form of such uniformly accelerated movement is given in that of a falling body whose velocity increases uniformly for successive time periods. We know that the force producing this movement is never less than the weight of the body, which remains constant from the time that it starts on its downward course. It is therefore evident that if we design for a movement of the body of uniform acceleration that the force required to propel it must be constant. It is immaterial in that respect, whether the movement be a translatory, as in

falling body. This curve is a parabola. To ascertain the velocity at any moment, we have only to determine the increment of the movement per unit time, or, expressed in other words, determine the differential quotient of this parabolic function at that moment. Both the geometric qualities of the parabola as well as the mathematical expression for its function lead to velocities which lie on a straight line emanating from the center

Geneva to 20 per cent in the five-slot Geneva, no means are possible by which to make a change anywhere between these two figures.

The four-slot Geneva, being universally adopted, precludes therefore the possibility of designing the machine for any other ratio of movement to rest, or darkness to light-transmission, than one to three.

In Fig. 3, the horizontal line denotes time, whereas the vertical lines may denote movement of the film. For the Geneva the movement is given by line *G*, which shows that from the beginning of engagement of the pin in the slot, the increase of the velocity of the film is extremely small; great increase in velocity, however, occurs at the point marked *h*. At the point *s* the velocity of the film has reached the maximum, and from there on decreases in velocity more rapidly during a short period *j*, and finally comes to zero on position plus 45.

It will be seen that the work of the Geneva is done almost entirely in the two short periods *h* and *j*, whereas little power is transmitted at the beginning or at the middle of the movement. The total strain of acceleration and the retardation of the film is therefore concentrated at two comparatively short periods of the whole time of movement and the wear of the Geneva slot and

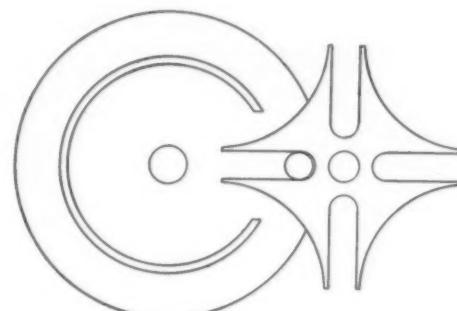


Fig. 2.—Four-slot Geneva movement.

of the co-ordinate system. In the diagram, Fig. 1, this velocity line is marked *v*.

In general, the force required to produce velocity changes is given by the increment of the velocity, which in case of the straight velocity line *v* is a constant designated *f* in the diagram, Fig. 1, as the increment of the velocity line *v* is the same for all the points of the diagram.

The object of the intermittent movement in a motion picture projecting machine is to advance the film in as short a period as possible with a minimum strain on the moving parts. The requirement of quick movement is evident from the fact that during the movement the shutter has to obliterate any possible light on the screen, and the longer the movement therefore the more the screen is deprived of useful light. On the other hand, the strain in moving parts has to be kept to a minimum to obviate undue vibration both of the machine and of

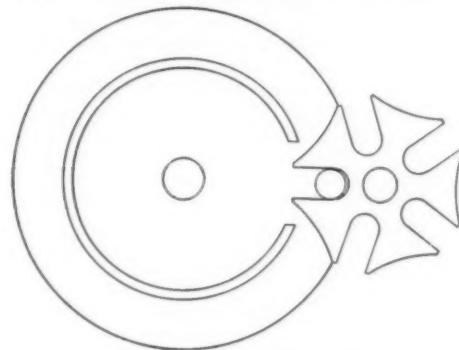


Fig. 7.—Five-slot Geneva movement.

pin as well as the intermittent sprocket's teeth and film holes becomes excessive.

To avoid such uneven and excessive force, both in the Geneva itself and on the film, Mr. Nicholas Power designed the cam movement, shown in Fig. 4.

This movement is not limited to any particular percentage for the movement of the film, the cam being designed for any number of degrees desired. The velocity of the film is diagrammatically shown in Fig. 5, which shows in comparison to Fig. 3 that the initial time of movement *m* is utilized to better advantage for accelerating the film and thereby relieving the part *h* of the diagram 3 of its excessive rise.

Such even distribution of power transmitted from the fly wheel to the intermittent, and from the sprocket to the film, accomplishes the total movement of the film of  $\frac{1}{4}$  inch at a shorter time, equal to 71 degrees of the fly wheel, with a strain on the film, which can be gauged by the comparison of steepness of the angle *a* as against the angle *A*.

To facilitate this comparison, Fig. 6 is shown wherein the movement as well as the forces required are shown

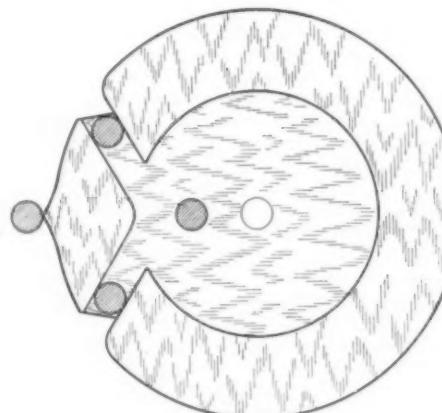


Fig. 4.—The Power cam.

the film, and to minimize the wear on the delicate part of the machinery and on the sprocket holes in the film.

It is deemed best to consider first the limitations of the intermittent movement generally known as Geneva movement.

In the Geneva movement the time required is exactly one quarter of the turn of the pin wheel. If the Geneva gear were made with five slots instead of four, as shown in Fig. 2, the movement would require one fifth of the revolution of the pin wheel; or, as it is usually expressed, in the four-slot Geneva, the movement and therefore of the film, covers 90 degrees of the fly wheel, whereas in a five-slot Geneva, the movement and therefore of the film, is completed in 72 degrees of the fly wheel.

With the five-slot Geneva, the movement of the film requires one fifth of the time and the film, while stationary, could transmit the picture during four fifths of the time. With the four-slot Geneva, the film is moving during one fourth of the time and standing still three fourths of the time.

While we could therefore shorten the percentual time of movement of the film from 25 per cent in the four-slot

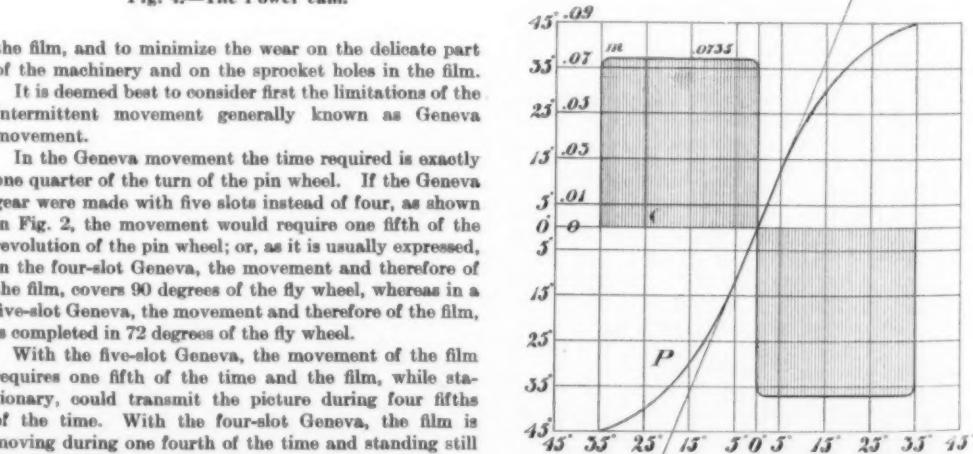


Fig. 5.—Movement of film as controlled by the new Power cam movement.

relating to those of the Geneva and the Power cam. Mr. Power has therefore combined in this one design three changes of mechanical operations:

1. Shorter time of movement (71 degrees as against 90 degrees.)

2. Uniform distribution of strain over the whole period of movement, as against the unevenly divided action of the Geneva.

3. Reduction in the engagement force from which three noticeable deserts are given in the operation:

1st. More light.

2d. Less vibration.

3d. Less wear both on the intermittent movement, intermittent sprocket and film.

An argument might be advanced that, as above men-

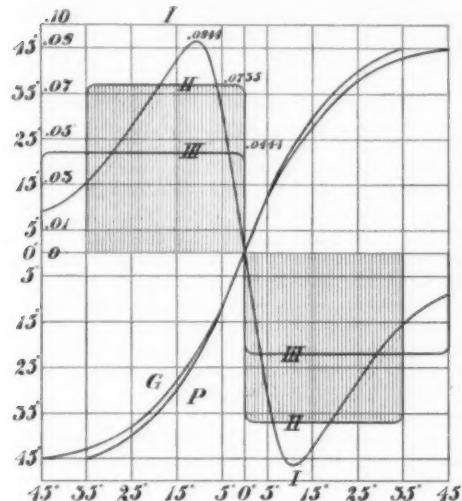


Fig. 6.—Comparison of movement and forces required by Geneva and Power movements.

#### Unit Coal\*

ATTENTION is called to the heat values for the "unit coal," the pure substance free from ash, moisture, sulphur, and other minor impurities. This value, like the coal-bed moisture may be regarded as the normal factor for the actual coal and does not vary in a given mine from year to year. If for example, the average unit value for a given mine is 14,350 British thermal units per pound of this material, any sample with whatever content of ash or moisture, when calculated to this "unit coal" basis, will give the same average value within the range of experimental error, or about 100 units in 14,000, a variation of less than 1 per cent. This value enables us to check the correctness of the various determinations, any one of which if seriously in error would vitiate the result. Conversely, by reversing the calculation we are enabled to obtain a close estimate of the heat value present for any given percentage of ash. This is of special value where it is desired to submit a bid for contracting in which a guaranteed heat value is to be indicated. The formula by which this value is derived is as follows:

$$\begin{aligned} \text{Dry B. t. u.} &= 5000S \\ \text{Unit B. t. u.} &= 1.00 - (1.08A + 55S) \end{aligned}$$

In which  $A$  is the weight of ash per gramme.

$S$  is the weight of sulphur per gramme.

If every mine operator were to obtain as often as possible this "unit" value for his product, he could very shortly derive from an average of his log of values, a basic factor which would be of great advantage to him in submitting propositions for coal supplies.

A special survey was recently made of certain mines in the five counties named in Illinois. The average of the "unit-coal" values for each mine may be taken as a constant for the output of that mine.

AVERAGE HEAT VALUE FOR UNIT COAL IN BRITISH THERMAL UNITS PER POUND.

No.	County	Coal bed	Number of samples averaged	Average—B. t. u. "unit coal"
1	Sangamon	5	15	14.424
2	Sangamon	6	5	14.340
3	Macoupin	6	6	14.310
4	Madison	6	18	14.350
5	Vermillion	6	19	14.597
6	Vermillion	7	9	14.730
7	Williamson	6	5	14.750

The use which can be made of these "unit" values such as are shown in this table may be readily under-

\* Bulletin 29, Illinois State Geological Survey, by S. W. Parr.

† Illinois State Geological Survey, Bull. 16, p. 212, 1909.

‡ Pillar and storage coal will have heat units from 1 per cent to 4 per cent below the values here given.

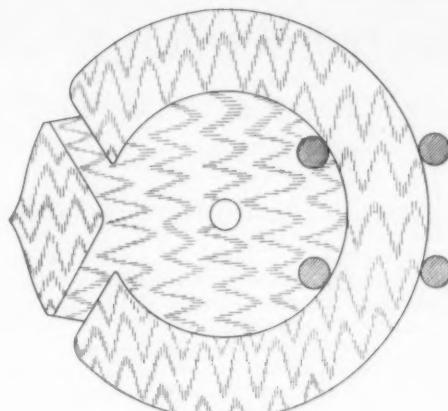


Fig. 8.—Another view of Power cam.

tioned, the Power cam shows more force transmitted during the initial part of the engagement than the Geneva movement, and in starting and therefore less destructive for the film, at least during this period of the engagement.

A rope will hardly last longer by being given plenty of rest mornings and evenings, but being overstrained beyond its safe capacity to a full day's work during the few hours of a day.

The work that the Geneva is not doing in the beginning of the movement, it has to make up during the short periods  $h$  and  $j$ , causing jerks and ruining the film, sprocket wheel and the slot and pin.

Comparing first the maximum force required for the Geneva with that of a Power cam of 90 degrees movement as given in III, we see that the latter requires a force which is less than one half of that required for the Geneva, the two absolute values being 0.44 as against 0.944.

Such great superiority of the Power cam enables us,

therefore, to reduce the time for its action and still remain with its actuating force below that of a Geneva.

Such case has been shown in Fig. 6 by force line II which corresponds to the cam as incorporated in the projection machines manufactured. There the time has been reduced from an angle of 90 degrees to only 70 degrees, thereby reducing the dark period. It is true that by such quicker action the actuating force increases but as seen from line II it is still far below the force required of the Geneva, the relative values being 0.735 against 0.944.

This comparison in Fig. 6 between the force line of the Geneva (I) and the Power cam as used (II), shows clearly the latter's advantage in reducing the time in a ratio of 70 degrees as against 90 degrees and reducing the actuating force in a ratio of 0.735 to 0.944.

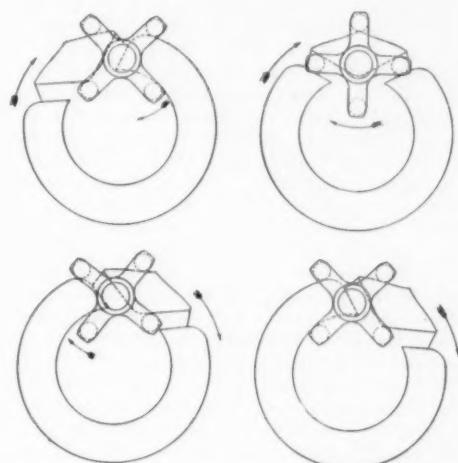


Fig. 9.—Diagrams illustrating operation of the Power cam.

a moisture factor of 15 per cent, the above value as derived for "dry" coal should be multiplied by 0.85, that is,  $12728 \text{ B.t.u.} \times 0.85 = 10818 \text{ B.t.u. per pound}$  of the "wet" coal, assuming a moisture factor of 15 per cent as indicated. In this connection attention should be given to the assumed values which it is proposed to maintain for water and ash.

#### Lightning Rods

EVEN to-day really few people understand what occurs when there is a flash of lightning, or the part played by the lightning rod. Some very interesting and valuable information on these matters and on the protective range of lightning rods is given by J. and J. S. B. Larmor in the *Proceedings* of the Royal Society. Among other things they say: "Electric discharge in a gas is a rupture along a line of force, and not over a surface. The initial rupture is to be expected at a place of maximum force, and spreads in both directions along the line of force through that point. In the case of a lightning rod the discharge would start at the summit of the rod, the place of most intense strain, and strike away from the rod. Once a line of disruptive discharge is established, the neighborhood of a lightning rod can have little effect, and a simple mathematical investigation shows that a thin isolated rod will draw the discharge hardly at all unless in the region around its summit, and that the modification in the field due to a thin rod is negligible along its sides unless close to it. It is the building carrying the rod which modifies the field and directs discharge to its own upper parts, which, therefore, need protection by conductors adequate to draw off this discharge to earth; and vertical rods, joining together, if need be, lower down, but rising from the corners of the structure to a height which need not exceed about half its breadth, will lift up the field of concentrated electric force from the region directly above the building to the region above their summits, and will so take the discharge. The rods may rise from an earth-connected network spread over the roof, but unless the meshes are fine enough to approximate to a complete metallic covering, it is questionable whether it would in itself protect a building from a discharge striking down upon it. A spread of connected metallic points some height above the building would appear to be more effective, and might even by themselves suffice to take up and guide away any likely stroke. In fact, if we neglect the discharge from the rods into the field, their effect is merely to provide the easiest and most probable path for such discharges as may be attracted by the structure. The discharge from the pointed extremities of the rods adds, of course, to the protective effect by slowly, but continuously, reducing the strain in their neighborhood, and therefore the liability to disruptive discharge."

## Electrometallurgy—II\*

### Modern Methods of Producing and Refining Various Metals

By Joseph W. Richards

Concluded from SCIENTIFIC AMERICAN SUPPLEMENT No. 2058, Page 379, June 12, 1915

We will next consider the question of the "fused salts." In nature we find a number of metals in the state of salts which are fusible and which can be electrolyzed—sodium, calcium, and magnesium are obtained directly by the electrolyzation of those simple salts. Common salt, for instance, is only worth a few dollars a ton. If converted into metallic sodium on the one hand and chlorine gas on the other, one worth several hundred dollars per ton, and the other worth fifty dollars a ton, you can see there is a great economic gain. The value of the product is out of all proportion to the cost of the raw material, and the cheapest way to do it is electrolytically. We have, therefore, numerous sodium works manufacturing sodium and chlorine from sodium chloride. Sodium fluoride is a stronger salt than sodium chloride, and if mixed with the latter is not decomposed by the current, because it is a weaker salt. The sodium fluoride keeps the melting-point of the bath down, and enables them to work it at a lower temperature, and thus get a better return of sodium. The uses for sodium increase greatly as the price goes down. Up to a couple of years ago sodium makers were using caustic soda ( $\text{NaOH}$ ), costing about forty dollars a ton. That was costly, and increased the price of the sodium; but by going back to the original sodium chloride, and finding electrolytic methods by which it could be utilized, the cost of the metal has considerably decreased.

Calcium chloride occurs to a small extent in nature, but should properly be classed as an artificial salt. We have here an interesting illustration of another method of electrolyzing a fused salt. The bath consists of the fused calcium chloride. Calcium is so light that it floats to the surface of the bath, and when it floats it is exposed to the air, and is apt to take fire. By putting the cathode just in contact with the upper surface of the electrolyte, the button is deposited against the electrode, and when it reaches a given size the electrode is lifted a bit. The fused salt sets on it and protects it from the air. By continuing to slowly raise the electrode, there is obtained an irregular rod of the metal. You buy the metallic calcium in a stick about one and one-half inches in diameter, just as it is drawn away from the surface of the electrolyte. Metallic magnesium is made in a similar way. With a specific gravity of 1.721 it floats to the surface. I have never seen any made in that way, but I hear that the same firm that makes calcium makes metallic magnesium in the same way.

Cerium is used for Welsbach gas mantles, which contain thorium and cerium oxide. The residue from this manufacture is piled up high in the Welsbach Company's yards at Gloucester. It is about half cerium oxide. Dr. Auer von Welsbach started to see if he could not utilize this residue, and he began by studying the properties of metallic cerium to see what useful properties it might have. He was impressed by the striking property which it has of giving sparks, and found by experiment that by alloying it with iron he could greatly increase the spark-giving property so as to make it useful in those little cigar-lighters with which we are all familiar. The alloy used in those lighters is made from the waste cerium oxides dissolved in fused fluorides. It is put into an electrolytic bath, in somewhat the same manner as a chloride. The other rare metals (lanthanum, didymium) are allowed to stay in because they do not injure the quality of the alloy. There is no works manufacturing cerium at the present time in this country; but I visited such works at Treibach, in Austria, last year, and I understand that Dr. Fettinger has been over here considering where to put up a plant to manufacture these alloys from the residues which are in the yards at Gloucester, N. J. This industry employs three or four thousand workmen in Austria, and there is no reason why we should not have a similar industry over here.

I mention zinc here because a great deal of money has been spent in trying to manufacture zinc chloride and then to electrolyze it. The idea is to treat those complex sulphide ores which contain zinc with chlorine gas, converting the zinc into chloride, separating it from the other chlorides, purifying it, and the forming of it a bath, electrolyzing it and getting back the chlorine, which is used again in the early part of

the process. The ores are so complex that the operation has not yet been made a commercial success.

Electrolysis of solutions in fused baths is a principle which was discovered by Mr. Charles M. Hall, and has been the foundation of the whole aluminum industry. It costs considerable money to get pure aluminum; but if you do not get it pure it is useless for many purposes. Mr. Hall was trying to decompose alumina ( $\text{Al}_2\text{O}_3$ ) electrically, and he conceived the idea that if he could find some fused salt which would dissolve it the problem might be solved. Cryolite from Greenland is used for that purpose. It looks like wax or ice; its name "cryolite," means "ice-stone." It fuses at 1,000 deg. Cent., and when fused it is as limpid or clear as distilled water. Alumina dissolves in it like sugar in water. Take such a solution, put electrodes in, pass the current through, and you get out aluminum. You have to replenish the alumina as the supply in the bath becomes depleted. This invention of Mr. Hall is the corner-stone of the whole aluminum industry. There is probably 150,000 horse-power being used to manufacture aluminum. The output last year was something like 65,000 metric tons, of which about 40,000 were manufactured in America. The extent of this infant industry is amazing; it replaces three to four times its weight of the metals with which it is competing, because of its very low specific gravity. The output of copper in this country is now about 500,000 tons a year, and is nearly stationary; while the output of aluminum, starting with almost nothing, has been doubling nearly every year. Last year, including Canada, the American output was estimated at 69,000,000 pounds. The commercial importance of this should appeal to us. I believe that aluminum is going to give copper a hard race. There is considerably more margin for reducing the cost of aluminum and selling it at a lower price than there is for copper. When copper gets below eleven cents a pound, many mines have to stop producing; but aluminum can be sold at a profit at a price lower than the cost of one equivalent amount of copper.

We now come to the electro-thermal methods and electric furnaces. The electric furnace was first used to fuse metals. There are different kinds of electric furnaces; you can class them broadly into resistance furnaces and arc furnaces. Resistance furnaces can be subdivided into the direct-resistance furnace and the induction furnace. The direct-resistance furnace is one in which the material is heated directly by the passage of the current through it, while in the induction furnace it is heated by an induced current. In the arc furnace, where you use the arc, there is also some heat generated by the resistance of the electrodes, and some by the passage of current in the materials, where the arc jumps to the materials. The resistance of the arc, however, will account for 75 to 90 per cent of the heat generated.

The fusion of metals was first tried by Siemens in England. He used a little crucible, making the bottom of his crucible one electrode of his furnace, and the other terminal an electrode entering from above. He published his paper before the Institute of Telegraphic Engineers in England, because he could find no other scientific society interested in it. He rigged up a little automatic regulator to keep the arc constant, and his idea was to melt steel directly in the crucible, a crucibleful at a time, by electric heat. In some of his tests he obtained about 50 per cent thermal efficiency for the purpose desired—i. e., the heat in the melted steel was some 50 per cent of the heat-equivalent of the electrolytic energy used. His furnace never went into commercial use; but it was followed some twenty years later by the furnace of Mr. Heroult in the Savoy, France, who was the first to have the idea of fusing steel in a large furnace. Girod also constructed a practicable steel-melting electric furnace, and there are several forms of successful induction furnaces. Within the next five years Mr. Heroult's resistance furnace will also be making steel. Electric-furnace steel is rapidly replacing crucible steel; it will probably replace it entirely in the next ten years. All steel could be benefited by a short sojourn in the electric furnace, and the latter will come into large use as an adjunct to the open-hearth steel furnace and the Bessemer converter.

Mr. Heroult's resistance furnace uses small pencil-shaped registers, filled with molten metal, and trans-

fers the heat generated in them to the molten metal bath. The circulation in and out of these registers is so active, because of the "pinch" force and its attendant "squirt" effect, that their temperature does not get excessive, and the heat generated in them is rapidly transferred to the main bath. I have seen this furnace working very prettily on brass and cast iron, and I believe it has as promising a future as any electric furnace.

The Stassano furnace is a typical arc radiation furnace. It is usually run by three-phase current, the three arcs being kept clear of the bath of metal, which is heated by direct radiation from the arc or indirect radiation from the roof. The three electrodes are a little above the surface of the bath, at equal angular distances and with an arc springing between them. But in practice the arc may easily pass to the bath because of the metallic vapors produced in an intense heat like that. The air in the furnace becomes quite conductive from silicon, manganese, and iron vapors, so that you can have a 6 inch arc with about 90 volts across the phases; it is similar to a mercury arc.

The induction-furnaces, of which there are several variations and types, are a great triumph of metallurgical and engineering art. I have the greatest respect for the man who first built a furnace like a transformer, with only one secondary turn, put a primary right in the center of that ring, and succeeded in keeping it cool enough so that it did not melt the insulation on the wire, and transmitting the magnetic flux through the intervening space and materials to the metal which was to be melted. I regard the induction-furnace as a marvel of engineering construction, and it was fortunate that it has been taken up by the Germans. It was first worked commercially in Sweden, but was devised years before by Mr. Colby, of Newark, N. J., who tried it, but did not make it a commercial success. Mr. Kjellin, in Gysinge, Sweden, did it commercially, and then the Germans took hold of it, and stuck to it, improved it, and with their great tenacity have overcome the difficulties and made the induction-furnace better than I think any other nation could have made it. Many have thought that the induction-furnace would drop out of the race, but the German is coming along with some further improvements all the time. It is better adapted for melting and keeping steel melted than for refining the steel. It is not very well adapted for refining the steel because of the limited surface exposed. The Germans, however, are overcoming even that difficulty, and have arranged a large open bath in the center of their furnace, a bath in the middle, where there is room for the action of the chemicals on the steel for refining it.

Mr. Paul Heroult was the first one to melt steel commercially in an electric furnace. He was not a steel-maker; he was an electrical engineer, and he used to say, "I do not know anything about steel, but I am going to learn." I think he succeeded by learning some short cuts. You know we frequently are handicapped by knowing too much about a thing. He made a new flux, and used the arc; he used it "without knowing that some things could not be done," and he did them. His furnace was nothing more nor less in outline than an open-hearth furnace. His idea was to build a tilting open-hearth furnace, and to put his two electrodes through the roof above the bath. The idea of putting two arcs in series, with the bath as an intermediate conductor, was novel. Heroult patented the idea of melting steel by two electrodes in an electric furnace, passing the two arcs through a layer of silica slag. Mr. Heroult's furnace has been improved upon or modified by Mr. Girod, who uses only one upper electrode and conducts this lower electrode through the hearth of the furnace, so that he has only one arc, and takes off the current through the one electrode running through the hearth of the furnace. These electrodes in action are partly melted, about half-way down, and the rest is solid. They are quite permanent; I have seen some of them which ran eighteen months. The steel metallurgist would be the last to dare to make a hole in the hearth of his furnace, and put an electrode through the bottom. But that was where the electrical engineer put it, and there has been no trouble whatever with those electrodes. Right where the electrical engineer put them would have been the last place the metallurgist would put them.

\* A paper read before the Engineers' Club of Philadelphia, U. S. A.

Concerning the reduction of compounds to metal in electric furnaces, I have time to pick out only a few characteristic examples:

Boron is one of the rarest metals, but its compounds are abundant. It is made by bringing a volatile boron salt with hydrogen gas into an electric arc, where they are heated to a very high temperature. The salt is reduced by the hydrogen to metal, and the vapors produced are chilled before they have a chance to recombine. It is the same operating principle as is used in the fixation of atmospheric nitrogen in Norway. This boron is being put on the market for use in casting "conductivity" copper. This is one of the most recent productions of the electric furnace.

In Niagara Falls, Mr. Tone is reducing ordinary silica sand,  $SiO_2$ , to metallic silicon. This gentleman once took me into the carborundum works at Niagara, showed me a barrel containing something, and told me to guess what it was. I made two or three vain guesses, and he finally told me that it was silicon, which, he said, "we can make for a few cents a pound." At that time metallic silicon was quoted in commercial price-lists at \$4 a gramme (\$18 a pound). He said he wanted to find some use for it. Silicon is somewhat volatile, and 25 per cent of that which he puts into his furnace goes up in smoke. He is now making silicon at Niagara Falls by the ton. Silica is mixed with carbon, put into a furnace heated by a carbon resistor, the mixture of silica and carbon being piled around this resistor and runs out something like slag. It is being cast into vessels for use in chemical works. Thus is the most abundant element on earth now commercially available at a price of about six or seven cents a pound. One can only speculate as to the future uses of it; it is made from the cheapest materials; the reducing agent is cheap carbon; and you have metallic silica from the electric furnace.

The zinc industry is attracting a great deal of attention. It is, apparently, one of the least progressive of the metallurgical industries. Little bits of retorts are heated to a high temperature, a few shovelfuls of roasted ore mixed with carbon are put into each retort and left there for 24 hours. Everything is done in a very homeopathic way, and yet it is so difficult a metal to handle that it is only by holding fast the ground gained that it has reached its present status. The electric furnace zinc industry has been made suc-

cessful in Europe; there are works in profitable operation in Norway, Sweden, and Finland, while much skillful experimenting has been done in America. Last year 4,000 horse-power was being used in producing zinc in Scandinavia, and 7,000 horse-power has been added since then. The firms are very reticent about their methods; in fact, there is no reliable published data about their present type of furnace.

The manufacture of ferro-manganese, ferro-tungsten, etc., for making special steels, is done almost entirely in the electric furnace. The oxide of iron is mixed with the oxide of the metal to be reduced, with sufficient carbon for reduction. It takes about half a horse-power year to produce a ton of 50 per cent ferro-silicon, for instance. The chief seat of this industry is the Savoy, in France, but the industry is gaining ground in the United States and Canada, and imports are decreasing. Stassano, in Turin, was the first to make such alloys, using his arc-radiation furnace, but enormous furnaces (Helfenstein's) of 5,000 to 10,000 horse-power are now used in this industry, which thus led up to the electric furnace manufacture of pig-iron and pig-steel.

The manufacture of the cheapest metal we have from the cheapest ore we have by electrometallurgical process is, I suppose, one of the greatest triumphs of electrometallurgy. The electric current can really be used for doing what is now done in the blast, and it is possible under some circumstances to replace it by an electrometallurgical furnace; that is the last triumph of electrometallurgy.

In one little place in Sweden that I visited two years ago, charcoal was getting scarce, and they were importing coke from England to run their blast-furnaces, and the quality of the product was not that of iron made with charcoal. They were much interested in the electric furnace, because it requires only one-third as much fuel to make a ton of pig-iron as the blast-furnace. In their blast-furnaces, with the charcoal available, they could make 300,000 tons of pig-iron, but in the electric furnace they could make 900,000 tons with the same fuel; so that was one of the inducements to use the electric furnace. The Swedes spent a quarter of a million dollars before they had a successful working furnace. They did their work in a most scientific way all through, watched their temperatures and all the conditions, and knew exactly what they were doing all the time. As a net result, they

made pig-iron in the electric furnace as cheaply as they can in their blast-furnaces. The Jern Kontoret (Iron Masters' Society) bought the patents for the furnaces, so that they became the common property of all the ironmasters of Sweden, and they have been putting up furnaces pretty rapidly. The last one was designed for 12,000 horse-power. It has been running for nearly a year at from 6,000 horse-power to 8,000 horse-power, making 55 tons of pig-iron per day. If it were run at full capacity, I think they could make 100 tons a day, which is equal to the average capacity of one of their blast-furnaces.

At Domnarfvet and Hagfors, in Sweden, the same thing is pending. At the latter works they calculate that with this large furnace there is a margin of \$2.50 per ton on the cost of pig-iron, to the advantage of the electrical furnace over their blast-furnaces, so that electric furnace pig-iron is being made at a profit and cheaper than it could be made in the blast-furnace in Sweden.

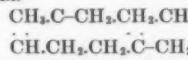
The possibility of making a product from this furnace which is not pig-iron, but which, as far as carbon content is concerned, will have to be classed as steel, has been proved. That product, with less than two per cent of carbon, is in reality impure steel, and not cast iron. It requires only a small amount of refining to bring it to pure steel. With the excess of iron ore present in the furnace you can make a low-carbon product. With electricity to furnish the heat, you can regulate the carbon so as to make a product with only two per cent of carbon. This is a possibility with an electric furnace; but it is not a possibility with the blast-furnace. We can thus make pig-steel, with less than two per cent carbon, which can be converted in the open-hearth furnace into pure steel in about half the time that the ordinary product of the blast-furnace takes. This will bring advantages with which the blast-furnace cannot possibly compete. In the case of the problem being worked out, pig-steel will replace pig-iron for the manufacture of steel; this opens up the possibility of the electric reduction of iron ore going into use in places where otherwise it would not go if the product were simply pig-iron. It may come into Canada or along our northern borders, where water-power can be obtained cheaply, for there is the large expenditure of 3,000 horse-power hours per ton of product to be reckoned with. This will be the next great advance in the electrometallurgy of iron and steel.

## Artificial Production of Caoutchouc\*

### Considerations of Synthetic Production of an Elastic Colloidal Substance

By F. Willy Hinrichsen, of the Koenigliches National-Pruefungsamt, Berlin<sup>1</sup>

THE question of the artificial production of rubber is a problem of the greatest commercial and scientific importance. The "synthetic rubber phantom" which for some time past greatly agitated the planters and all interested in the collection of wild and plantation rubber, is still so present in the memory of all, that it hardly seems necessary to dwell here upon the commercial importance of rubber synthesis. On the other hand, from a purely scientific viewpoint there was presented the problem of preparing for the first time, synthetically, a typical colloidal substance and to discover relations between chemical constitution and elastic properties. It is therefore evident that the above problem was eagerly approached from various angles of science and technology. While I am here giving a short review of the present state of this subject I must at the same time limit myself to several essential main points. Complete consideration of the subject is, of course, out of the question, since only a small portion of the work accomplished in the technical laboratories on this subject is made publicly available. After Harries<sup>2</sup>, in his pioneer work of 1905, established that the chemical constitution of natural caoutchouc  $C_{10}H_{16}$ , as a 1,5-dimethyl-cyklooctadien of the formula



it was easier to approach the synthesis of the interesting hydrocarbon from the basis of the newly discovered knowledge. Several earlier observations had been made. Thus, Bouchardat<sup>3</sup> had found that the hydrocarbon isoprene,  $C_4H_6$ , resulting from the dry distillation of caoutchouc, and which had been previously discovered

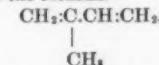
by Williams,<sup>4</sup> was a colorless liquid which boiled easily and which could be converted into a rubber-like substance by polymerization in the presence of aqueous hydrochloric acid. Tilden<sup>5</sup> had also found that, in the same way, isoprene which, in addition to being formed from caoutchouc, is produced by passing oil of turpentine through red hot tubes, was converted by hydrochloric acid or nitrosylchlorid into caoutchouc. However, as in spite of many repetitions under varying conditions of experimentation by other investigators, and even by Tilden himself, it was no longer possible to obtain the same result; it was assumed that only a purely accidental observation had been made, and that the material obtained, which in the state of science then existing, could not be determined to be caoutchouc, was not really a caoutchouc and that the statements of Bouchardat and Tilden were based on errors.

As a result of the enormous increases of the prices of rubber during the last few years and also because of the zealous scientific attention to the caoutchouc problem, particularly by Harries, the attention of a large circle of people, particularly in the industries, was drawn to the problem of the synthetic production of caoutchouc. The result was, that Fritz Hofmann and Carl Coutelle,<sup>6</sup> chemists of the Elberfeld Farbenfabriken vorm. Bayer & Co., succeeded in 1909 in converting absolutely pure isoprene, which they obtained by a new method, into caoutchouc, by simply heating it in a closed tube, either by itself or in the presence of certain other substances. A sample of this caoutchouc was sent to Harries, who proved with certainty by chemical tests that in this case caoutchouc actually resulted. Since the process by which Hofmann and Coutelle worked was not yet known, Harries also took up the experiments on the conversion of isoprene into caoutchouc, and in March 1910 he re-

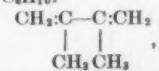
ported in a lecture in Vienna<sup>7</sup> on his observations, stating that it is possible to convert isoprene into caoutchouc by heating it in a closed tube in the presence of glacial acetic acid. Harries deserves the credit for being the first to publish a process which could be repeated, for converting isoprene into caoutchouc.

After the ball had once been started rolling investigations were also begun by others attacking the problem. Particular credit should also be accorded especially in the technical interpretation of the problem in addition to the Elberfeld Farbenfabriken, to numerous individual native and foreign investigators, and of industrial establishments, the Badische Anilin und Soda-fabrik of Ludwigshafen.

Even in the original patent specifications of the Elberfeld Farbenfabriken the raw material was not limited to isoprene, but a series of hydrocarbons of related constitution was included in the scope of the observation. Isoprene itself has the formula



It contains two neighboring double bonds, a so-called system of "conjugated double bonds." Other compounds with conjugated double bonds, as was recognized by Hofmann and Coutelle from the start, also possessed as does isoprene the same property of polymerizing into caoutchouc-like substances. Among these we have for example, erythrene,  $C_4H_6$ :  $CH_2 \cdot CH \cdot CH \cdot CH_2$ ; further dimethylbutadiene,  $C_6H_{10}$ :



and many other similarly constructed substances.

Aside from the fact that because of the varied natures of the raw materials there was possibility of obtaining a whole series of different caoutchoucs, which of course must differ from each other because of their chemical

\* *Zeitschrift des Vereins deutscher Ingenieure*, 1915, vol. 59, p. 16. See also Hinrichsen and Memmler: *Der Kautschuk und seine Pruefung*, published by S. Hirzel, Leipzig 1910; pp. 20 et seq. Ditmar: *Die Synthese des Kautschuks*, published by Th. Steinkopff, Dresden 1912.

<sup>1</sup> *Ber.*, 1904, vol. 37, p. 2,708; 1905, vol. 38, p. 1,195.

<sup>2</sup> *Compt. rend.*, 1875, vol. 80, p. 1,446; 1879, vol. 89, p. 1,117.

<sup>3</sup> *Proc. Royal Soc., London*, 1860, vol. 10, p. 516.

<sup>4</sup> *Chem. News*, 1882, vol. 46, p. 120.

<sup>5</sup> German Patent Applications F. 28,390. Class 39b Group 1. September 11th, 1909. German patent 235,423, September 30th, 1909. German Patent 235,686, December 28th, 1909.

<sup>6</sup> *Gummi Ztg.*, 1910, vol. 24, p. 850.

constitution, it was also noticed that the process of polymerization itself was susceptible of variation and that caoutchouc prepared in various ways from the same raw material would differ from each other.

Harries<sup>8</sup>, and independently of him the English investigator Mathews and Strange<sup>9</sup>, simultaneously observed that the polymerization in the presence of metallic sodium took place with great velocity, but that the caoutchouc obtained was different from that obtained by heating alone. Furthermore, the chemists of the Badische Anilin und Sodaefabrik found that the results were different when the polymerization with sodium was carried out in a carbon dioxide atmosphere. Another process which was developed in the Badische Anilin und Sodaefabrik depends on the use of ozonides or peroxides as catalysts.

According to the kind of raw material and the method of polymerizing, rubbers are obtained which vary from one another totally in their properties. The following summary gives, according to Holt's<sup>10</sup> statements, a brief

CAOUTCHOUCS FROM BUTADIENE, $C_4H_6$ .			
Normal caoutchouc (by heating): easily soluble, elastic, vulcanizable.	Ozonid caoutchouc: insoluble, swells up greatly, very elastic, unvulcanizable.	Carbon dioxide caoutchouc: insoluble, does not swell up, moderately elastic, unvulcanizable.	Sodium caoutchouc: easily soluble, elastic, vulcanizable.
Normal caoutchouc: easily soluble, elastic, vulcanizable.	Ozonid caoutchouc: swells up greatly, only soluble after rolling, elastic, vulcanizable.	Carbon dioxide caoutchouc: insoluble, does not swell up, elastic, vulcanizable.	Sodium caoutchouc: easily soluble, not elastic, difficultly and incompletely vulcanizable.
Normal caoutchouc: easily soluble, not elastic, can only be vulcanized to hard rubber.	Ozonid caoutchouc: swells up, only soluble after rolling, not elastic, can only be vulcanized to hard rubber.	Carbon dioxide caoutchouc: insoluble, does not swell up, not elastic, difficultly vulcanizable, easily oxidizable.	Sodium caoutchouc: soluble and insoluble modification, not elastic, unvulcanizable.

review of a series of such varying caoutchouc-like substances.

The scientific significance of the above-mentioned facts is obvious. It was the first time that elastic colloidal materials were synthetically prepared. The possibility of obtaining materials having changing properties by changing the raw material and the polymerization process, that is, by choice of the experimentation conditions, led to the hope that it must be possible, as in the field of dyestuffs and odoriferous substances, arbitrarily to obtain materials of definite properties by means of slight changes which would be particularly suitable for definite purposes. Just as we are able, in the case of dyestuffs to change the tone of the dyestuff at will by the addition of certain groups, etc., so it should also be possible in a similar way to arbitrarily change the elastic and solid qualities of caoutchouc.

It is entirely different as regards the economic importance of the synthesis of caoutchouc. Should artificial rubber become a serious rival of natural rubber it must equal it in two respects: price and technical adaptability. It is not necessary, however, to conceive of the complete replacement of natural rubber by artificial, as in the case of indigo, alizarin, etc.

As regards the price of synthetic caoutchouc, this is first of all governed by the cost of preparing the hydrocarbons of the isoprene series which serve as the raw materials. In this respect great progress has undoubtedly been made in the most recent times. A process of the Badische Anilin und Sodaefabrik which depends on certain fractions of petroleum seems to promise special success.

Additional raw materials are among others, starch, amyl alcohol, oil of turpentine, acetylene, etc. In spite of the great pains that have been taken in order to increase the yields of the various processes, it must be said that the desired goal has not yet been reached. As regards the price of a serious competition of the artificial with plantation rubber is not yet to be thought of. In addition also the amount of oil of turpentine which would be required, is limited and its price would soar with an increasing demand. In order to secure the starch necessary for the world's demand of rubber, which already amounts to more than 100,000 metric tons yearly, fields of corn or potatoes would have to be planted, the extent

of which would have to very greatly exceed that of the present rubber plantations. From all these processes there will result such large quantities of by-products, that their removal would give rise to even more difficult problems than that of producing the caoutchouc itself.<sup>11</sup>

Even in spite of the last named difficulties the question of price would not be the controlling one if the previously mentioned objects were accomplished and if it were possible to produce by the proper choice of working conditions caoutchouc-like materials specially adapted for certain purposes. It can be imagined that certain synthetic caoutchoucs designed for definite purposes, embodying a combination of certain favorable properties may surpass natural caoutchouc and may be sold at a higher price. This has not yet been achieved.

No sufficient technical data have yet been made public regarding the technical adaptability of synthetic caoutchouc. As far as known observations on this subject go, it is evident that synthetic caoutchouc has not approached the properties, especially the stability of natural

### Cost in Cement Manufacture

The cost of power required in the manufacture of Portland cement reaches a higher percentage of the total cost of production than in most any other industry; and investigations seem to show that, when properly operated, there is little difference in the power required by different types of machines used in the processes. It is therefore evident that any reduction in the costs must be in the direction of the power used, and it is believed that the application of electric power can be made to materially reduce the expense of manufacture.

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<sup>8</sup> Ann., 1911, vol. 383, p. 188.

<sup>9</sup> Compare Harries: Z. angew. Chem., 1912, vol. 25, p. 1,458.

<sup>10</sup> Z. angew. Chem., 1914, vol. 27, p. 158.

<sup>11</sup> Compare F. Hoffmann: Z. angew. Chem., 1912, vol. 25, p. 1,462.

<sup>12</sup> Ber., 1914, vol. 47, p. 360. See also Harries, ibid. p. 573. Steimigg, ibid. p. 852.

